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URANIUM DEPOSITS OF THE SOUTHERN PART OF THE SAN JUAN BASIN, NEW MEXICO[1]

LOWELL S. HILPERT AND ROBERT H. MOENCH

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[1] Publication authorized by the Director, U. S. Geological Survey.

ABSTRACT

Since 1950 about 50 million tons of uranium ore has been discovered along the southern margin of the San Juan Basin, New Mexico. Here the exposed sequence of sedimentary rocks ranges in age from Permian to Cretaceous, and is associated with intrusive and extrusive rocks of Tertiary and Quaternary age. The uranium deposits are separable into three types—those in sandstones and associated mudstones of the Entrada and Morrison formations of Jurassic age, and Dakota sandstone of Cretaceous age; those in the Todilto limestone of Jurassic age; and one deposit in a pipelike structure in the Morrison formation. The deposits in the clastic sediments are similar to most of the uranium deposits in other parts of the Colorado Plateau region in type and habit of ore and accessory minerals, in the tabular form of ore bodies, and in their association with some form of carbonaceous material. The deposits in limestone have a somewhat similar mineral assemblage to that of the other deposits in the region but are unique in the type of host rock and their preference for structurally deformed beds. The pipelike deposit is unique.

Although igneous activity has been intense in the eastern part of the area from late Tertiary to Recent time, there is no evidence to suggest a genetic relation between the igneous activity and the uranium deposits. In fact, what are probably the oldest exposed igneous rocks intrude and displace the deposits.

Three periods of deformation are recognized. The first was during the time between the accumulation of the Entrada and Dakota sandstones, the second in the early to middle Tertiary, and the third in the middle to late Tertiary. Only structures of the first period show an obvious influence on the distribution and localization of the uranium deposits. From the pattern or frequency of distribution of the known deposits, and on the basis of interpretations from known geologic relations, the deposits seem to be clustered in a zone at least 20 miles wide north of the present outcrop. This zone is called the southern San Juan Basin mineral belt. Although the concept of this zone, or belt, restricts the favorable ground geographically, the amount of unexplored ground within the limits of the belt is enough to contain several times as much uranium resources as are now known.

INTRODUCTION

THE discovery, in 1950, of a uranium deposit on the southern margin of the San Juan Basin in northwestern New Mexico prompted intensive exploration that by 1958 had found about 50 million tons of ore reserves, classed as available, and worth at least a billion dollars at the current (1958) price schedule. The known deposits are in an area about 20 miles wide extending from Gallup to Laguna, a distance of about 85 miles (Fig. 1). The name "southern San Juan Basin mineral belt" is suggested for this area.

This paper briefly summarizes the general geologic relations of these deposits, speculates on the origin and localization of some individual deposits and the entire belt, and attempts to appraise the chances for additional discoveries. Although some new evidence and interpretations are presented, space does not permit a detailed description of the deposits and the inclusion of all evidence to support the interpretations. A much shortened version of the report was originally prepared for publication in the Proceedings of the

United Nations' Second International Conference on the Peaceful Uses of Atomic Energy. The present paper gives a more complete description of the geologic relations and, through this publication, is planned to reach those who do not have ready access to the Proceedings of the Second International Conference.

This presentation is based largely on the results of areal and mine mapping that was done in the Laguna district (Fig. 2) by R. H. Moench and associates between July 1955 and May 1958, and on regional reconnaissance and specialized studies by L. S. Hilpert and associates between July 1954 and May 1958.

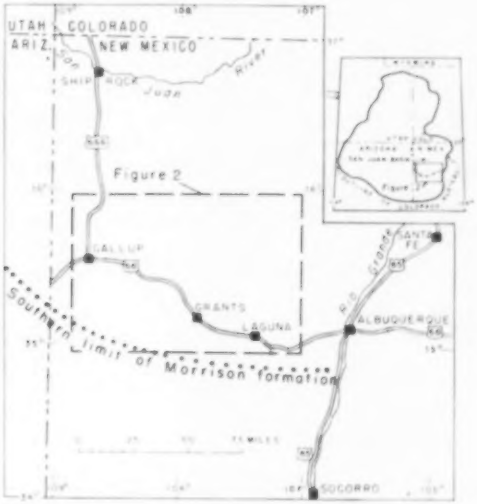


FIG. 1. Index map of northwestern New Mexico, showing the outline of Figure 2.

GENERAL GEOLOGY

The San Juan Basin is a structural unit covering an area of about 15,000 square miles in northwestern New Mexico (Fig. 1). Rocks exposed along the southern margin consist of sedimentary strata ranging in age from Permian to Cretaceous inclusive, and associated with intrusive and extrusive rocks of Tertiary and Quaternary ages. The sedimentary rocks generally dip northward at low angles toward the center of the basin, but this regional attitude is modified locally by faults and minor folds.

STRATIGRAPHY

All productive uranium deposits along the southern margin of the San Juan Basin are in sedimentary rocks of Jurassic and Cretaceous age. The lithologic characteristics and variations in thickness of these strata and the

stratigraphic distribution of the uranium deposits are summarized in Table 1. More detailed descriptions of the Todilto limestone and the Morrison formation, both of Jurassic age, are given below, for these two formations contain most of the deposits in the region.

Todilto Limestone

The Todilto limestone is gray and has a fetid odor when freshly broken. Except where coarsely recrystallized, it is fine-grained and thinly bedded in the lower part and medium-grained and massive in the upper part.

In the central and eastern parts of the southern San Juan Basin mineral belt, where the Todilto limestone is ore-bearing (Fig. 2), the Todilto averages about 20 feet in thickness, but ranges considerably in thickness locally. In many places the limestone beds are conspicuously deformed by folding and faulting; most of this deformation is entirely within the formation, but in some places a few feet of beds above and below the formational contacts are disturbed, thus causing abrupt though small changes in the thickness of the formation. In the Laguna district the Todilto is several feet thinner than average on the crests of broad small amplitude folds of Jurassic age and is correspondingly thicker than average in the troughs of these folds.

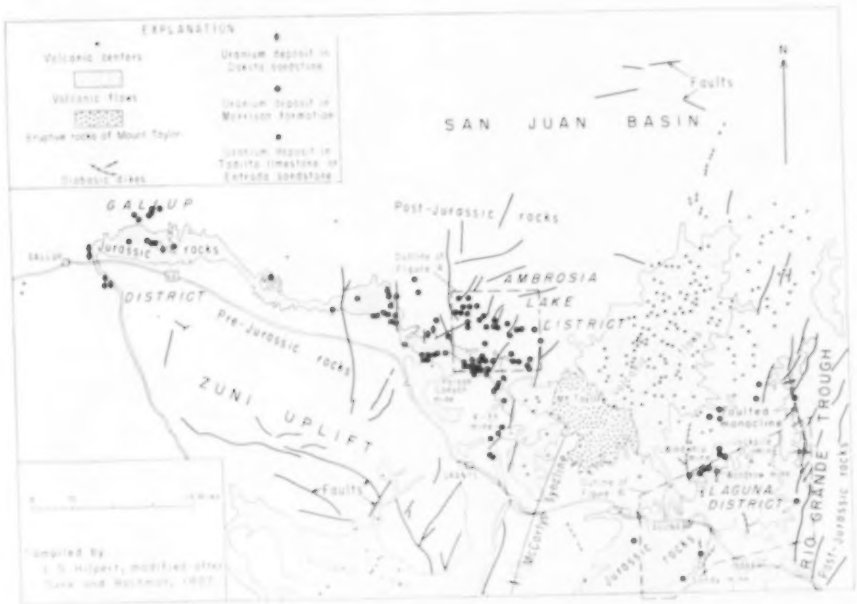


FIG. 2. Geologic map of the southern part of the San Juan Basin and vicinity, showing the uranium deposits and outline of Figures 4 and 6.

TABLE 1

SEQUENCE OF FORMATIONAL UNITS CONTAINING URANIUM DEPOSITS ALONG THE SOUTHERN PART OF THE SAN JUAN BASIN, NEW MEXICO

System	Formation	Thickness (feet)	Character and distribution	Uranium deposits
Cretaceous	Dakota sandstone	5–100	Fine- to medium-grained quartz sandstone, locally conglomeratic. Generally carbonaceous shale and locally coal at base.	Some small deposits, generally near base and in close relation to carbonaceous material.
—Unconformity—				
Jurassic	Morrison formation	0–600	Brushy Basin member; dominantly a greenish-gray claystone and, locally, thick arkosic sandstone units. Contains Jackpile sandstone (of local usage) at top in Laguna district. Ranges from 0 feet at Gallup to about 500 feet in thickness north of Laguna.	Significant deposits in sandstone beds in Ambrosia Lake and Gallup districts. Largest deposits and greatest reserves in Laguna district occur in Jackpile sandstone.
			Westwater Canyon member; arkosic, fine- to coarse-grained sandstone and some claystone lenses. Ranges from 300 feet in thickness north of Gallup to discontinuous lenses in Laguna district. Poison Canyon sandstone (of local usage) is tongue of Westwater Canyon in Brushy Basin.	Contains largest deposits and greatest reserves in Ambrosia Lake district. Also moderately large deposits in Gallup district.
			Recapture member; fine- to medium-grained, friable sandstone and some silty claystone beds. Occurs in distinctive alternating light-gray and reddish-brown units 5–10 feet thick. From 20–170 feet thick; absent at least locally in Laguna district.	Contains no significant deposits.
	Bluff sandstone	175–330	Fine- to medium-grained quartz sandstone. Dominantly a thick-bedded unit with some relatively thin interbedded siltstone units near the base.	Contains no deposits.
	Summerville formation	100–220	Fine-grained sandstone beds, generally 1 to several feet thick, alternating with thinner beds of siltstone.	Contains a few small deposits, only where underlying Todilto limestone is mineralized.
	Todilto limestone	0–85	Fetid dense gray laminated limestone; massive in upper part. Ranges from pinch-out near Gallup to maximum thickness in Laguna district. Includes an upper unit of anhydrite and gypsum in Laguna district that ranges from discontinuous masses at south to continuous unit to the north.	Contains small to fairly large deposits. Most are in Ambrosia Lake district. The anhydrite-gypsum member is barren.
	Entrada sandstone	150–250	Reddish-orange fine-grained quartz sandstone; lighter colored at top. Generally thins eastward. In Laguna district two distinct units—a lower reddish-orange unit and an upper white unit.	Contains a few small deposits in Laguna and Ambrosia Lake districts—all at top of formation.

The Todilto limestone pinches out southward along a west-trending line about 12 miles south of Laguna and 15 to 20 miles south of Grants, and it pinches out westward along a north-trending line several miles east of Gallup. The formation is as much as 85 feet thick in the northern part of the Laguna district, where its upper part is composed of anhydrite and gypsum.

Except where it is strongly deformed and recrystallized, the Todilto limestone in the Ambrosia Lake district can be separated into three stratigraphic zones; from bottom to top these are commonly referred to by the miners as the "platy," "crinkly," and "massive" zones. The lower two zones are about equal in thickness and constitute about half the total thickness of the formation. The "platy" and "crinkly" zones consist of fine-grained, thin-bedded limestone with thin partings of siltstone; black, dense, carbonaceous material is conspicuous locally along the partings in the "crinkly" zone. The bedding in the "platy" zone is generally undisturbed, whereas that in the "crinkly" zone is intensely crenulated. The "massive" zone consists of more coarsely crystalline limestone with indistinct bedding. In many places this zone is a breccia of limestone fragments, mostly cemented by calcite. Locally the top of the "massive" zone is a breccia, with fragments of limestone embedded in sand derived from the overlying Summerville formation. The upper part of this zone also contains lenses of siltstone, indicating a gradational contact with the overlying Summerville. In the Laguna district the part of the Todilto below the "massive" zone contains a sequence of beds that has characteristics of both the "crinkly" and "platy" zones, but that is not separable into these two units as it is in the Ambrosia Lake district.

Uranium deposits occur in all three stratigraphic zones in the Todilto. Probably most deposits are in the "platy" or "crinkly" zones, but they may occur in any one or in any combination of the three zones. The deposits are all localized where the limestone beds are deformed by folding and faulting, most of which is entirely intraformational.

Morrison Formation

The Morrison formation ranges from less than 100 to as much as 600 feet in thickness in the area of the southern San Juan Basin mineral belt. This formation extends over a broad region to the north, northwest, and northeast of this area, but a short distance south of the area the Morrison has been removed by pre-Dakota erosion. Here the Dakota sandstone rests unconformably on progressively older beds south of the mineral belt area.

The Morrison comprises three members—the Recapture, Westwater Canyon, and Brushy Basin members—that have partly ill-defined or gradational contacts. The Recapture member is the lowest, and it consists dominantly of sandstone with some silty claystone beds. The sandstone is fine- to medium-grained and forms alternating light-gray and reddish-brown units 5 to 10 feet thick. The Recapture member is absent locally in the Laguna district, but it is as much as 170 feet thick elsewhere in the mineral belt area (Fig. 3).

In some places along the southern margin of the San Juan Basin the

Westwater Canyon member—the middle unit of the Morrison formation—can only be separated from the overlying Brushy Basin member arbitrarily. Both contain beds of similar lithologic types but in different proportions. The Westwater Canyon member is composed dominantly of light-colored fine- to coarse-grained arkosic sandstone, with some claystone like that in the Brushy Basin. The Brushy Basin member is composed dominantly of greenish-gray claystone, with some sandstone similar to that in the Westwater Canyon. In addition these two members intertongue. The Poison Canyon sandstone (of local usage), for example, is a tongue of the Westwater Canyon member in the Brushy Basin member (Fig. 3).

With this approach, the Westwater Canyon member is conceived as thinning eastward from a thickness of 300 feet near Gallup to discontinuous lenses near Laguna. The Brushy Basin member, on the other hand, ranges in thickness from 0 near Gallup to about 500 feet north of Laguna.

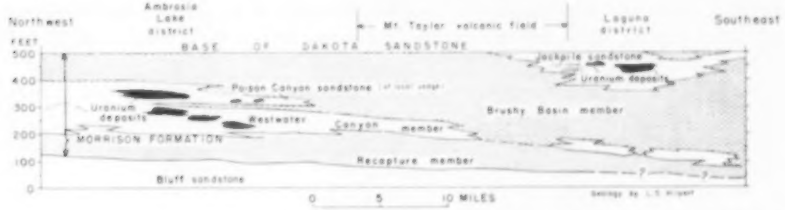


FIG. 3. Diagrammatic geologic section showing the uranium deposits and stratigraphic relations of the Morrison formation between the Ambrosia Lake and Laguna districts, New Mexico.

As presently used, the Jackpile sandstone (of local usage), which is exposed only in the Laguna district, is included in the Brushy Basin member. It forms the uppermost part of the member, and is as much as 190 feet in thickness. According to J. S. Schlee (14, p. 1793, and oral communication) the Jackpile sandstone is a fluvial "shoestring" sand about 10 miles broad with distributary-like channels to the northeast. The unit trends northeasterly across the Laguna district, and sedimentary structures indicate that these fluvial sands were transported northeasterly, parallel to the length of the unit.

The important ore-bearing sandstones are generally in thick layers, with crossbedding dominantly of the fluvial type, and they are intercalated with relatively thin and discontinuous lenses of claystone. The sandstones are mostly fine- to medium-grained, but are locally conglomeratic, and they are dominantly feldspathic. The sandstones similar to those in the Westwater Canyon and the lower parts of the Jackpile sandstone are cemented by silica, calcite, and lesser amounts of clay, but the upper part of the Jackpile sandstone is mostly clay-cemented. Fragments of fossil tree trunks and limbs are also present in the sandstones; they are commonly silicified, but some are coalified. A fine-grained black carbonaceous material that is uranium-bearing is abundant in the uranium deposits; it impregnates the sandstone, and

probably was introduced after the sands accumulated (*see* section on deposits in clastic sediments).

The sandstones of the Westwater Canyon and Brushy Basin members, except the Jackpile, are typically yellowish gray to light grayish red, but near ore deposits they have been altered to light gray. The Jackpile sandstone, on the other hand, is dominantly light gray to nearly white: its lighter color probably resulted from weathering before the overlying Dakota sandstone was deposited. The Jackpile and other beds in the upper part of the Brushy Basin were truncated by erosion before the Dakota accumulated.

Electric log data from the few holes that have been drilled north of the Ambrosia Lake mining district suggest that the sandstone of the Westwater Canyon member there is more uniform in thickness and character and contains less mudstone than in the mining district. This difference may indicate a northward change to more uniform conditions of sedimentation. As the host sandstones of the Morrison formation in the mining district are characteristically variable in texture and composition, this possible change in conditions of sedimentation may have produced a rock that is less favorable for the localization of ore.

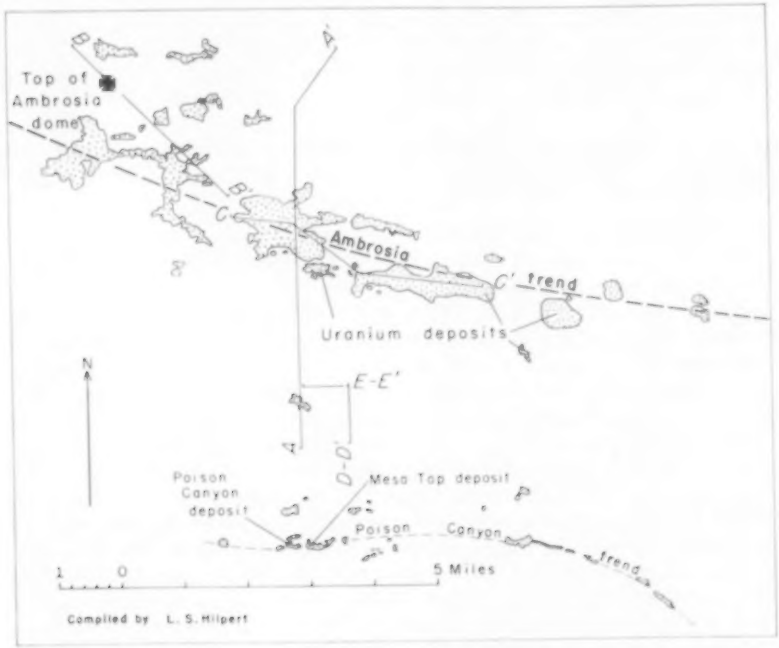


FIG. 4. Map of part of the Ambrosia Lake district, showing location and approximate outline of the uranium deposits in the Morrison formation, and lines of sections shown in Figures 5 and 7. See Figure 2 for location of area.

Nearly all the known uranium deposits in the Morrison formation in the mineral belt area are in sandstone beds in the sandstones of the Jackpile and Westwater Canyon. The Westwater Canyon member contains the largest deposits in the Ambrosia Lake district and moderate-sized deposits in the Gallup district. Some deposits in the Ambrosia Lake district are in the lower part of the Brushy Basin member, whereas those in the Laguna district are in the Jackpile sandstone near the top of the unit.

Deposits in the Ambrosia Lake district are distributed mainly in two elongate groups—the Ambrosia trend, containing the largest deposits in the district, and the Poison Canyon trend (Fig. 4). Section A-A′ of Figure 5, which is drawn north-south across the Ambrosia trend, shows that the bulk of the deposits are grouped near the central part of a thick sandstone mass. This sandstone mass perceptibly thins and tongues into the Brushy Basin mudstones both north and south of the group of deposits. On the other hand, in sections B-B′ and C-C′ (Fig. 5), which are longitudinal to the Ambrosia trend, the sandstone mass appears to be more uniform both in thickness and in lithologic continuity than in section A-A′, except over the Ambrosia dome. These relations suggest that the deposits of the Ambrosia trend are in the central, relatively thick part of a sandstone mass that is elongated in an easterly to southeasterly direction, and that this elongate mass of sandstone is responsible for the belt-like grouping of the deposits. Likewise, the deposits of the Poison Canyon trend seem to be localized in the central part of an east-trending sandstone unit (7, 8, 2, 3; Mathewson, written communication, 1953).

In the Laguna district the deposits in the Jackpile sandstone are not distributed in as clearly defined belts, and the Jackpile uranium deposit is elongated about at right angles to the dominant northeasterly sedimentary trends. The known deposits, however, are grouped in a broad zone near the central and thickest parts of the Jackpile sandstone.

STRUCTURAL GEOLOGY

The sedimentary strata along the southern margin of the San Juan Basin generally dip northward at low angles, but they are broken by faults and joints, and warped by gentle folds; some units are deformed locally by intraformational folds, faults, and collapse structures. Although some individual structural features cannot be dated with complete confidence, three general periods of deformation are recognized since the accumulation of the Entrada sandstone, the oldest formation of Jurassic age in the area. The first period was chiefly during Jurassic time but may have extended into Early Cretaceous time, the second in the early to middle Tertiary, and the third during middle to late Tertiary. Only structures of the first period show an obvious influence on the distribution and localization of the uranium deposits.

The first period of deformation produced two sets of folds and probably the smaller structures that appear to be associated with them. Figure 6 illustrates the distribution of these folds and smaller structures in the Laguna district. Here one set of folds consists of broad, gentle warps that generally trend easterly, but are sinuous. The largest of these warps is perhaps several

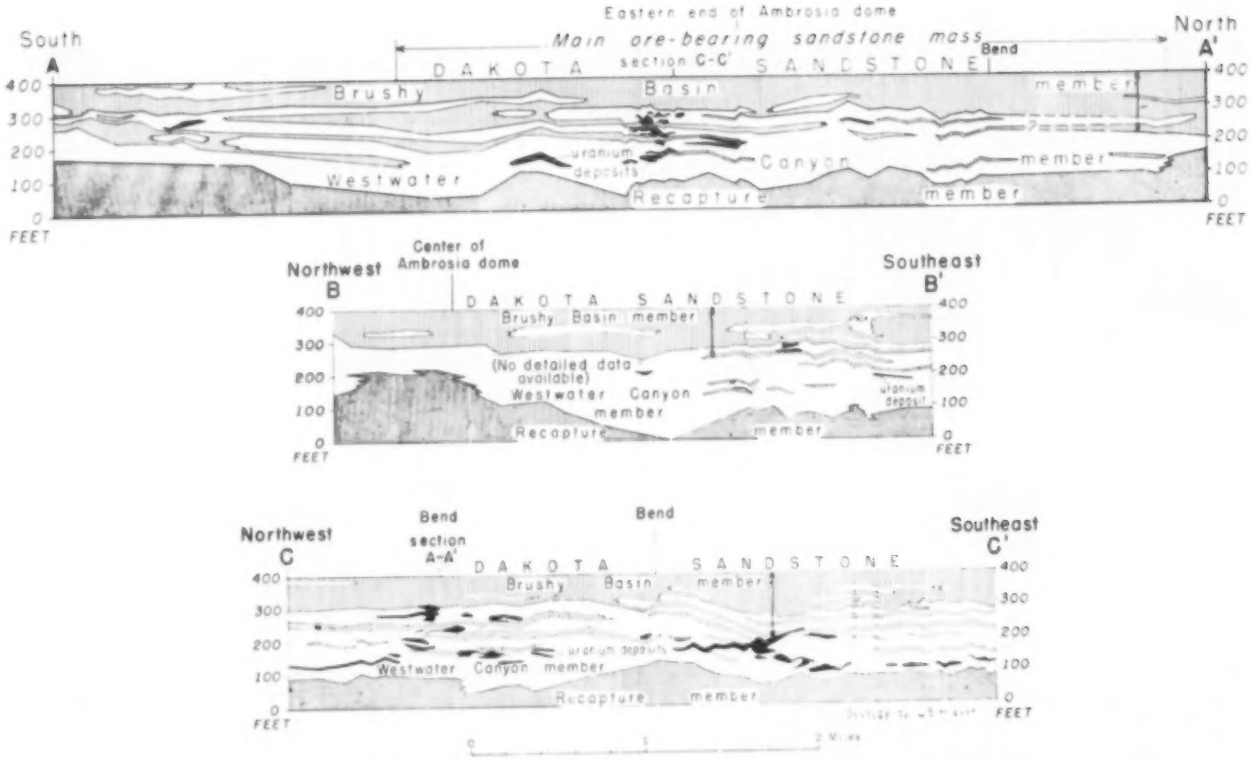


FIG. 5. Diagrammatic geologic sections of the Morrison formation in the Ambrosia Lake district showing the relations of the uranium deposits to the stratigraphic units and to the Ambrosia dome; post-Dakota folds removed.

miles wide, and has an amplitude of a few hundred feet. In the Laguna district this set of easterly trending warps contains the largest folds of the Jurassic fold system and is termed the major set. This set is essentially parallel to the northern margin of a broad highland that existed in central and southern New Mexico in Jurassic time (13).

A similar set of folds probably also exists in the Ambrosia Lake district. Section D-D′ of Figure 7 drawn north-south between the Poison Canyon and Ambrosia trends (Fig. 4), shows a set of broad folds in the sandstone and claystone layers of the Morrison formation; the Morrison is overlain with angular unconformity by the Dakota sandstone. In section E-E′ (Fig. 7),

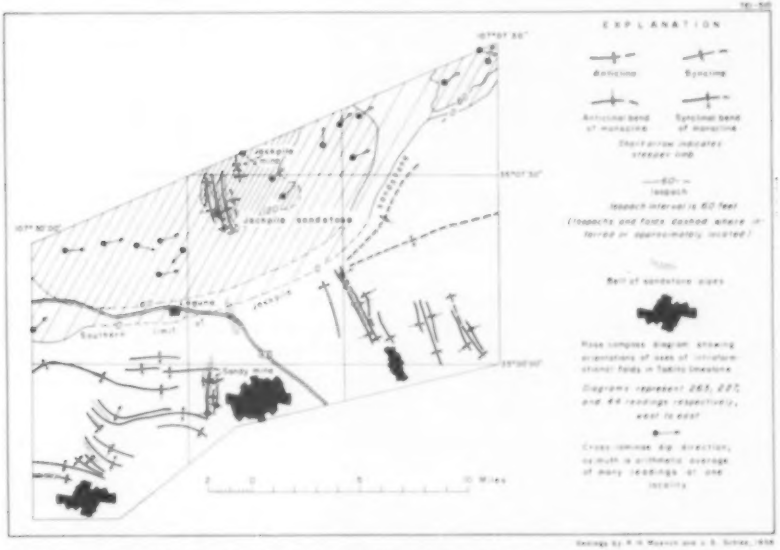


FIGURE 6.—GENERALIZED GEOLOGIC MAP OF PART OF THE LAGUNA DISTRICT, NEW MEXICO, SHOWING THE ELEMENTS OF THE JURASSIC STRUCTURES, AND THICKNESS OF THE SOUTHERN PART OF THE JACKPILE SANDSTONE (OF LOCAL USAGE)

drawn east-west in the same area, the Dakota sandstone appears to overlie the Morrison formation conformably, and no pre-Dakota folds are apparent. Section E-E′, therefore, is essentially parallel to a set of easterly-trending pre-Dakota folds, and section D-D′ is normal to this set of folds. In addition the sandstone and claystone layering in the Morrison seems to be more uniform and continuous in an easterly direction, parallel to the trend of the folds (section E-E′) than in a northerly direction (section D-D′), a relation similar to that expressed by the Westwater Canyon sandstone mass in the vicinity of the Ambrosia trend.

The Ambrosia dome (Fig. 4) is a prominent structure that involves the Dakota and younger rocks, and is, therefore, in part a younger structure.

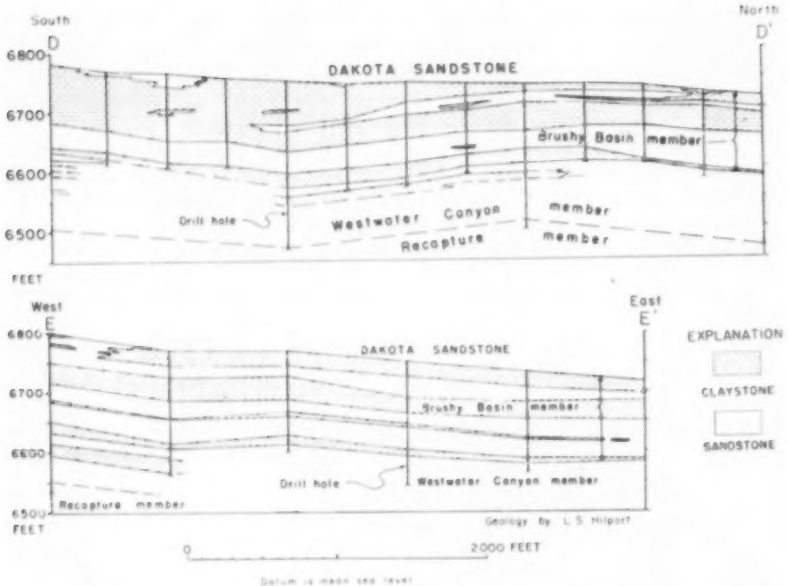


FIG. 7. Geologic sections showing local north-south and east-west stratigraphic and structural relations of the units of the Morrison formation north of the Poison Canyon mine, Ambrosia Lake district.

However, section B-B′ (Fig. 5) shows that the Westwater Canyon member thins markedly over the crest of the dome, and that it is relatively thick around the entire periphery of the dome. It is doubtful that the thinning of the Westwater Canyon member over the dome resulted from differential compaction because claystone of the Brushy Basin shows no similar thinning over the crest of the dome. It seems more likely, therefore, that the dome was a positive or relatively high domal feature in Morrison time, and received less sand over its crest than around its periphery.

The second set of Jurassic folds is well developed in the Laguna district (Fig. 6). Most are about a half a mile across, with amplitudes of as much as 100 feet, and they trend persistently N. 10°–30° W. They are much smaller than the largest folds of the easterly-trending set and are termed the minor set of the Jurassic fold system. For lack of exposure the intersections between folds of this set and the easterly-trending set were not seen, but both sets of folds may occur in the same areas.

The bedding of the Todilto limestone is contorted in many places in the area. Where strongly disturbed, the beds are folded into a great variety of shapes—as open and closed anticlines, fan folds, recumbent folds, and chevron folds, most of which are asymmetric. Although parts of the folds are fractured, and some folds are cut by small low-angle thrust faults, the characteris-

tics of plastic deformation are dominant. The amplitude of these structures is about equal to, or somewhat less than their breadth, which ranges from less than an inch to about 30 feet. Most of the folds are confined to the Todilto limestone, although some of the largest folds involve beds in the top few feet of the underlying Entrada sandstone and basal beds of the overlying Summerville formation. At least in the Laguna district these folds in the Todilto limestone are localized mainly along the flanks and troughs of the broad east-trending and north-trending folds, and their dominant trends are likewise eastward and northward, as indicated by the rose compass diagram in Figure 6. The folds in the Todilto limestone in the Ambrosia district also trend dominantly northerly and easterly, but their relations to the broad pre-Dakota folds has not been determined. As the Todilto limestone in the Laguna district is somewhat thicker in the troughs of the broad folds than on the crests, these data combined suggest that the intraformational folds developed by flowage of poorly consolidated muds down the limbs of the broad folds. This flowage occurred under some sedimentary cover as none of the folds is truncated by bedding planes.

Peculiar collapse structures are common in the Morrison formation and in the Bluff and Summerville formations in the area. They are circular in plan and vertical in orientation, and they range from 1 inch to 200 feet in diameter and from 1 foot to 300 feet high. Locally they are called "sandstone pipes" or "breccia pipes." One of the several hundred pipes found in the area is known to contain uranium ore, that at the Woodrow mine. (See Fig. 14 and section titled the Woodrow deposit.) Subsequent to the field work for this report the pipe that is exposed in the Jackpile mine has been found to be mineralized to some extent (Figs. 8 and 9).

Typically the pipes are bounded by a ring fault, or by several concentric ring faults and the beds surrounding the pipes are commonly inwardly downwarped (Figs. 8, 9, and 14). The material at any point in a pipe consists of the same material that forms the wall rock a short distance above, but it has been largely disaggregated and shows little or no bedding or other sedimentary structure. The pipe-filling material is compact and without voids other than the pores of the rock. The pipes flare upward and are covered by undisturbed beds. Downward, though their bases are rarely seen, they likewise pass into undisturbed beds. Typically the pipes terminate at their tops in sandstone, and extend downward into mudstone or siltstone. The pipes are largely confined to two stratigraphic assemblages: the Morrison formation, and the Summerville formation and the lower part of the overlying Bluff sandstone. None is known to penetrate the Todilto limestone or the Dakota sandstone. Their general stratigraphic range, therefore, is about 1,000 feet.

The tops of some pipes are well exposed and provide a basis for determining their time of origin. Figure 8 is a section through the top of a pipe in the Jackpile sandstone. The general characteristics of this pipe are similar to those described above, but in particular it illustrates the upward flare of the top, and shows that it both cuts and is overlain by Jackpile sandstone.

In addition this pipe contains abundant and diverse types of fragmental carbonaceous material, whereas the wall rocks are essentially barren of carbonaceous material. The writers believe that this pipe formed during the deposition of the Jackpile sandstone, and was buried by additional Jackpile sandstone. It probably formed rapidly, sucking into it much plant debris from its immediate surroundings at the surface. The plant debris probably was thus buried and preserved, whereas in the wall rocks it was not. Other pipes reveal unconformable relations between the downwarped sandstone at their tops and the overlying undisturbed sandstone, indicating that they formed at the time of sedimentation of the units that contain them.

From the observations made so far, no satisfactory interpretation can be offered to explain the origin of these collapse features. They evidently formed during the accumulation of the highest beds they cut, and before complete

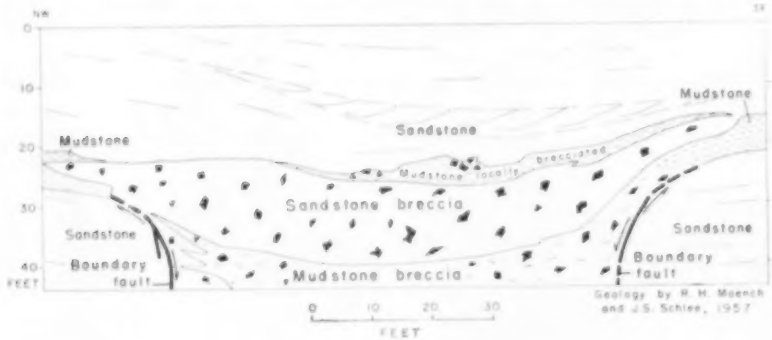


Figure 8.--Section through top of sandstone pipe in Jackpile sandstone (of local usage), Jackpile mine (along line N 53°W.)

compaction and consolidation of the beds containing them. Most of the pipes in the Laguna district are localized in long narrow belts that closely parallel the Jurassic folds of both sets (Fig. 6), suggesting that this deformation influenced the collapse in some way.

The Jurassic folds of both the easterly- and northerly-trending sets formed prior to the deposition of the Dakota sandstone, and possibly contemporaneously with the deposition of the Jurassic rocks above the Entrada sandstone. Folded rocks in both the Laguna and Ambrosia Lake districts are truncated in many places by the overlying Dakota sandstone, demonstrating the pre-Dakota age of the folds. As the sandstone pipes originated during the deposition of the Summerville, Bluff and Morrison rocks, and are commonly localized in belts that closely parallel the folds, it is likely that the folds developed in part at the same time. In addition, as the intraformational folds in the Todilto limestone probably resulted from flowage of poorly consolidated

lime down the flanks of the broad folds, it is likely that the broad folds developed in part not long after Todilto deposition.

If the Jurassic folds developed contemporaneously with the deposition of the Jurassic rocks, more likely than not the folds influenced the deposition and distribution of these rocks. The sandstones of the Morrison formation in both Laguna and Ambrosia Lake districts are interpreted to have been thus influenced. The Jackpile sandstone, in the shape of a channel sand, roughly parallels the major easterly-trending set of Jurassic folds; the data on cross-lamination suggest that the sands were transported in the same direction (Fig. 6). In addition, the thickness of the Morrison formation beneath the Jackpile sandstone increases by as much as 150 feet from the margin of the channel to its center. It is possible, therefore, that in the vicinity of the channel sand the Morrison formation occupies a broad northeast-trending warp that formed contemporaneously with the deposition of the Morrison, and that the stream that deposited the Jackpile sandstone was controlled by this warp.

In the Ambrosia Lake district pre-Dakota folding may have likewise influenced the deposition of the Morrison formation. It has been noted previously that the sandstone and mudstone layering are most continuous and uniform in thickness in an easterly direction, which is essentially parallel to the elongation of the sandstone host of the Ambrosia trend. It has also been noted that at least one set of pre-Dakota folds in this district has an easterly axial trend. It is possible, therefore, that broad gentle folding during Morrison time tended to localize into easterly courses the streams that deposited the sandstones.

The second period of deformation was in early to middle Tertiary time. Uplift again occurred in the area of the Zuni Mountains and subsidence in the area of the San Juan Basin defined this structure. The beds tilted into low-angle northerly to northeasterly dips west of the Mount Taylor area and northerly to northwesterly dips on the east side. The McCartys syncline formed and many faults and folds developed near the eastern end of the Zuni uplift. The Ambrosia dome, which probably started to form before the Dakota sandstone was deposited, became well defined. The faulted monocline that marks the western boundary of the Rio Grande trough (Fig. 2) may also have formed at this time.

The third period of deformation took place during middle to late Tertiary, and possibly into Quaternary time, when the Colorado Plateau province was uplifted regionally and the Rio Grande trough subsided. In the region of the southern San Juan Basin mineral belt this deformation was characterized dominantly by fracturing. To a limited extent fracturing took place during the two earlier deformations, but as middle to late Tertiary was the time of greatest differential movement between the Rio Grande trough and the Colorado Plateau, this was probably the time of most intense fracturing in the mining districts. The joint and fault system in the Laguna district is similar to that on the western edge of the Rio Grande trough, and the late Tertiary and Quaternary igneous rocks are fractured by the same system.

Although some geologists believe that the fractures of post-Dakota age influenced the localization of the uranium deposits along the southern margin of the San Juan Basin—and certainly these fractures had some influence on the distribution of secondary minerals—the writers believe that these structures formed later than the primary mineralization. Where post-Dakota faults intersect ore deposits they cut and displace the ore. Some fractures carry ore minerals of uranium and vanadium, but only where the fractures cut ore deposits, and where such deposits show obvious effects of oxidation. Furthermore, where the distribution and trend of deposits show a suggested parallelism or association to fracture systems, the occurrences invariably seem to be above the present water table where there has certainly been some oxidation and redistribution of uranium.

RELATIONS OF URANIUM DEPOSITS TO IGNEOUS ROCKS

Igneous activity was intense in the eastern part of the Gallup-Laguna area from late Tertiary to Recent time. It probably began with the intrusion of diabasic sills and dikes, followed by the formation of Mount Taylor, a large stratified volcano, and closely followed by sporadic outpouring of basaltic lava from a great many pipes and fissure vents in the immediate vicinity of Mount Taylor.

Diabasic sills and dikes east of Mount Taylor interconnect and probably were intruded contemporaneously, but are not accurately dated. The dikes dominantly follow the prominent north-trending fracture set, and the sills, in turn, are jointed and locally faulted by the same set. This suggests that the diabase was intruded contemporaneously with fracturing that occurred mostly in middle to late Tertiary time. Inclusions of the diabase were found in a volcanic pipe that probably supplied one of the earliest basaltic flows, indicating that the diabasic rocks are at least older than what may be the oldest basaltic flows. These basaltic flows were extruded essentially contemporaneously with the latest stages of the Mount Taylor eruptions. Because the entire Mount Taylor sequence probably formed over a short period of time, the writers suspect that the diabasic intrusions took place before both the basaltic and Mount Taylor extrusions.

The volcanic rocks of Mount Taylor consist dominantly of pyroclastic rocks and flows of rhyolite, trachyte, and latite, and also dikes of porphyritic andesite (9). The basaltic flows, pipes, and fissure vents in the immediate vicinity are composed dominantly of olivine basalt, but include some rocks of intermediate composition. Both the Mount Taylor stratovolcano and the oldest basaltic flows rest on an erosion surface that is probably younger than the major structural developments in the Rio Grande trough. The oldest basaltic flows are probably overlain by some of the pyroclastic rocks from Mount Taylor, and overlying basaltic flows intertongue with an alluvial cone built out from the upper part of Mount Taylor; these relations suggest little, if any, break in time between the Mount Taylor eruptions and the extrusion of the basaltic flows. Younger basaltic flows rest on younger erosion surfaces, and some flows follow the present drainage.

The distribution pattern of the known deposits in the entire mineral belt area does not suggest a spatial relation to the igneous rocks (Fig. 2). Furthermore, the diabasic dikes and sills, probably the oldest igneous rocks, intrude and displace many uranium deposits in the Laguna district (Figs. 11 and 17) and metamorphose them along the contacts. As these rocks are younger than the deposits, it is unlikely that they influenced the localization or origin of them.

URANIUM DEPOSITS

Along the southern margin of the San Juan Basin the uranium deposits are separable into three types—those in sandstones and associated mudstones of the Entrada, Morrison, and Dakota formations; those in the Todilto limestone; and one deposit in a pipelike structure. The deposits in the clastic sediments are similar to most of the uranium deposits in other parts of the Colorado Plateau region in type and habit of ore and accessory minerals, in the tabular form of ore bodies, and in their association with some form of carbonaceous material. The deposits in limestone have a somewhat similar mineral assemblage to the other deposits in the region but are essentially unique in the type of host rock and their preference for structurally deformed beds. The pipelike deposit is truly unique in the area, though similar in some respects to the deposit in the collapse structure at Temple Mountain, Utah, and perhaps a few other occurrences in down-faulted rocks.

In spite of the differences in stratigraphic position and the lithologic and structural environments of the deposits in the southern part of the San Juan Basin, the writers believe that they all belong to the same general class and had a common origin. The geologic relations that are a basis for this idea, and certain other geologic relations that will be described, permit the concept of a mineral belt along the southern margin of the San Juan Basin.

Mineralogy

The ore minerals are dominantly fine-grained, and they mainly occupy pore spaces in the host rock, but also partly replace it. These minerals consist of low-valent uranium and vanadium minerals and their oxidized products. Fine-grained carbonaceous material is abundantly and intimately associated with the ore minerals in some and perhaps all the deposits. Other accessory minerals consist of fine-grained sulfides in all deposits and fluorite in some. The uranium in many of the deposits is in part or largely in the hexavalent state, especially in those deposits that are above the present water table. It is assumed that this hexavalent uranium formed by oxidation of minerals containing tetravalent uranium. The occurrence of only the unoxidized ore minerals and the carbonaceous material will be described in detail.

Ore Minerals.—Coffinite is a uranium silicate with the approximate formula of $U(SiO_4)_{1-x}(OH)_{4x}$ (17). It is black, moderately hard, moderately heavy, and can be distinguished from uraninite only by its X-ray pattern. In the southern San Juan Basin area it is apparently the principal uranium mineral in unoxidized ores in sandstone. Typically it is extremely fine-grained

and intimately associated with the carbonaceous material, mostly occupying pore spaces but partly replacing the sand grains. In the Woodrow deposit (see below), on the other hand, some coarse-grained coffinite that is apparently free from carbonaceous material has been found.

Uraninite (UO_2) is the common uranium mineral in the unoxidized deposits in the Todilto limestone. It is typically fine-grained. It mainly impregnates and replaces the limestone, in part as fine intergrowths with fluorite and a vanadium-bearing silicate (11, 12). It is also localized along siltstone laminae between bedding planes in the limestone. Uraninite has been recognized in a deposit in the Entrada sandstone, where it occurs as thin films on sand grains, in veinlets in a vanadium-bearing silicate, and as small concretions surrounded by pyrite.

As the vanadium content of the deposits in the southern San Juan Basin area is low, averaging about 0.15 percent V_2O_5, vanadium minerals are not conspicuous. Most of the low-valent vanadium in these deposits, however, occurs as a fine-grained micaceous mineral and is presumed to be one or more varieties of the vanadium-bearing silicates—mica, chlorite, or clay—that are common in the vanadium-bearing uranium deposits in other parts of the Colorado Plateau region. This material mainly occupies the pore spaces of the rock or replaces argillaceous material and detrital quartz and feldspar. Haggite and paramontroseite, both vanadium oxides, have also been reported as mineral occurrences.

Tyuyamunite [$Ca(UO_2)_2(VO_4)_2 \cdot 7\text{–}10\frac{1}{2}H_2O$] and carnotite [$K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$] are two common secondary uranium minerals where vanadium is available. Other common secondary uranium minerals are also present in places. These minerals mostly occur in open spaces, either pores or fractures.

Carbonaceous Material.—The sandstones containing most of the deposits in the southern San Juan Basin area are light-colored but the ore is colored various shades of gray. Three suites of samples from the Jackpile and Windwhip deposits, totaling 21 samples, reveal a close correlation between blackness, as determined by the Rock-color chart,[2] and organic carbon content: The darker the rocks the higher the organic carbon content. Very light-gray [2] rock, typical of barren host sandstone, contains 0.04 to 0.08 percent organic carbon; and the darkest sample—medium dark-gray to dark-gray [2]—reveals 2.16 percent organic carbon (Wayne Mountjoy, analyst). A suite of 52 samples from the Jackpile mine gave the following average assays: light-gray samples 0.04 percent U_3O_8; medium-gray samples, 0.31 percent U_3O_8; and dark-gray samples, 0.41 percent U_3O_8. As the organic carbon occupies much more volume than the equivalent weight percent of uranium and is at least as abundant by weight as uranium in these samples, the gray color of the samples and the ore is probably imparted by the carbonaceous material.

X-ray studies of the ore in sandstone show that much of the uranium is in the form of finely divided coffinite that is dispersed through the carbonaceous

[2] Rock-color chart, 1951, Geological Society of America.

material. This carbonaceous material is apparently ubiquitous within the deposits, so its distribution reflects the gross form of the deposits. Most of it occurs as coatings on sand grains and intergranular fillings. Locally it is massive and partly replaces the detrital grains. Where coarse enough to separate mechanically from the rock it is a black brittle substance with a submetallic lustre and a specific gravity of about 2.

Accessory Minerals.—Pyrite and marcasite are the common accessory minerals in all deposits, but they are generally sparse. These minerals mostly form minute crystals, irregular patches, or small nodules in the sandstone, partly replacing the sand grains. In the Woodrow deposit, on the other hand, pyrite and marcasite are much more abundant and form small incomplete replacement masses and locally boxwork structures controlled by the intersections of bedding and fracture planes in breccia fragments.

Trace amounts of fine-grained chalcopyrite, galena, and sphalerite are also present in many deposits.

Fine-grained fluorite, partly intergrown with uraninite, occurs as disseminated specks and in small irregularly shaped masses in places in deposits in the Todilto limestone.

Deposits in Clastic Sediments

The uranium deposits in clastic sediments have yielded most of the ore produced and contain most of the known ore reserves in the southern San Juan Basin mineral belt. Most of the deposits are in sandstone lenses in the Morrison formation; a few are in the Entrada sandstone and a few are in sandstone and carbonaceous shale of the Dakota sandstone. The deposits in the Dakota have been described by Gabelman (5, p. 422–429; 6, p. 303–319) and will not be discussed here.

The ore-bearing sandstones are fine- to coarse-grained, they are composed dominantly of quartz but contain various amounts of feldspars and other minerals common in sandstone as well as clay particles and thin mudstone layers. The ore and associated minerals, including the fine-grained carbonaceous material, impregnate the sandstone, mostly occupying pore spaces but also partly replacing the sand grains. The ore bodies mostly occur as tabular layers that lie essentially parallel to the major bedding but which in detail transect bedding. These bodies are irregular in plan but tend to be elongate parallel to the trends of sandstone lenses, other sedimentary structures, and the two sets of pre-Dakota folds. They may be as much as several thousand feet in length and 50 feet or more in thickness. Small masses only a few feet across may be tabular or irregular in shape and roughly equidimensional.

Carbonized or silicified plant fossils are present in the Morrison formation in the southern San Juan Basin, but unlike many uranium deposits in other parts of the Colorado Plateau region, these fossils are not particularly abundant in the ore-bearing sandstone, and they are not conspicuously more abundant in the mineralized rock than in the surrounding barren sandstone. The plant fossils in the ore are commonly richly mineralized; but such materials a few feet above the ore are commonly barren of uranium. The possibility that this

plant material influenced the localization of the deposits seems less likely in northwestern New Mexico than in other parts of the Plateau region.

On the other hand, many ore deposits and possibly all the larger ore deposits contain much uranium-bearing organic carbon in the form of a black fine-grained material that is disseminated through the sandstone and coats and partly replaces the sand grains. The distribution of this material is apparently reflected by the gross form of the uranium deposits. Because the deposits assume a variety of forms that cut across sandstone bedding and crossbedding, as shown in Figures 10, 12, and 13, it is assumed that the organic carbon was introduced into the sandstone in a fluid form. As the deposits composed of this material are commonly at some level above the base and below the top of the sandstone, as shown in Figures 9 and 13, it was probably introduced under some kind of water-table or fluid interface condition. The rather close association of this carbonaceous material and the uranium it contains suggests they were introduced at the same time.

Deposits in Limestone

The Todilto limestone is fine- to medium-grained, but where it has been deformed it is partly recrystallized and coarse-grained. The ore minerals and the associated sulfides and fluorite are dominantly fine-grained, and they occur as replacements disseminated in the rock and along minor fractures and bedding planes. The ore bodies are localized where the limestone has been deformed by intraformational folding and faulting. Some ore bodies are irregular in shape but most are elongate and range from 20 to 30 feet in width and from 100 to a few thousand feet in length. Although most of the ore is in the lower part of the Todilto limestone, it may occur throughout the formation, and thus the ore bodies range in thickness from a few feet to as much as 20 feet or more. In a few places the ore bodies extend into the top few feet of the underlying Entrada sandstone or a few feet into the overlying Summerville formation.

The Todilto limestone is dark-colored, has a fetid odor, and contains as much as 1 percent or slightly more organic carbon. Some carbonaceous material is obviously concentrated as a dense black substance along parting planes in the thinly bedded parts of the formation, but some of it probably is disseminated throughout the rock. It is not obviously more abundant in or near ore than in the barren rock away from deposits. Analyses of the mill-pulp samples from 23 deposits showed a range from 0.05 to 0.14 percent organic carbon in the ores (Wayne Mountjoy, analyst). No data are available on the adjacent barren host rocks. More information is needed regarding the nature and distribution of this carbonaceous material and its possible influence on the localization of uranium minerals.

Deposit in a Sandstone Pipe

As only one deposit in a sandstone pipe, that at the Woodrow mine, has been observed in northwestern New Mexico, the description of it will be deferred to the section of this report where individual mines are described (see below).

Relations of the Deposits to Structural Features

Sedimentary structures in sandstone, intraformational folds and faults in the Todilto limestone, pipelike collapse structures in sandstone and mudstone, and tectonic folds formed by regional deformation all influenced the localization of the uranium deposits. As far as the writers can determine, the only tectonic structures, however, that have directly or indirectly controlled the deposits are those that are related to the Jurassic, or first, system of deformation.

Many ore deposits in the Morrison formation are in or near the central thick parts of sandstone lenses, and they tend to be elongate parallel to the trend of these lenses, suggesting that these parts of the lenses offered channelways for the ore-bearing solutions and favorable loci for ore deposition. Although such features as bedding planes, mudstone layers, cross-laminae, and grain-size variations within small sedimentation units show concentrating effects within deposits, sedimentary structures alone have localized only a few deposits. Commonly deposits transect sedimentation units within the host rocks, and the group of deposits in the Sandy mine area crosses the Todilto limestone-Entrada sandstone contact (Fig. 15). Likewise, many of the minor forms assumed by the ore within deposits sharply transect the sedimentary structures.

As all the deposits in the Todilto limestone are associated with intraformational folds and faults, these structures apparently controlled the deposits. Likewise, the Woodrow—the only deposit in a sandstone pipe—was obviously localized by the structure it occupies. Although the top and bottom of the Woodrow pipe, the only pipe definitely known to be ore-bearing, are not visible, there is no definite evidence that this pipe or any of the others are connected with any other vertical structure that might have formed a through-going channelway for ascending or descending solutions. Thus, even though the Woodrow pipe certainly localized its deposit, its function may have been that of a locus of ore deposition rather than a channelway for solutions.

The folds resulting from regional deformation of Jurassic age probably caused and localized intraformational flowage of beds in the Todilto limestone and perhaps triggered the slumping in the sandstone pipes, and may also have had some controlling influence on the position and direction of flow of the streams that deposited the ore-bearing sandstone lenses in the Morrison formation. If true, these folds had an indirect influence on the localization of the uranium deposits. With regards to later deformation, on the other hand, the writers have found no positive evidence that the positions or trends of deposits are in any way related to folding or fracturing. Furthermore, all through-going faults observed appear to have displaced the deposits. Although in places enrichment has occurred along regional faults and fractures within deposits, secondary concentration, of relatively recent age, seems to have been the more likely cause.

Localization and Origin

The writers can offer only general suggestions regarding the localization and origin of the uranium deposits in the southern San Juan Basin mineral belt area. Although the three types of deposits certainly were localized by different controls, the writers favor the idea of a common origin. The deposits in the Morrison formation are in the central parts of sandstone lenses, form tabular layers that commonly transect bedding at low angles, and consist of an intimate mixture of ore minerals and carbonaceous material. An organic solution moving along the beds under water-table or fluid interface conditions conceivably could form deposits of this character if some local influence caused precipitation of constituents in solution. The same or a similar solution moving along the Todilto limestone and adjacent beds might have found conditions favorable for uranium precipitation in the limestone where it was deformed and partly recrystallized. In a somewhat similar manner the Woodrow pipe could have served as a locus for precipitation of uranium from passing solutions. No definite evidence as to the source of the ore-bearing solution or the metals contained is recognized. The deposits certainly formed after Jurassic deformation, probably after the Dakota sandstone was deposited, and before pronounced deformation in Tertiary time.

Jackpile and Satellitic Deposits

The Jackpile uranium deposit, in the Laguna district, is probably the largest single deposit in the United States, and is one of the world's great producers of uranium. It constitutes about one third of the total known uranium ore reserves in New Mexico, but its average grade is probably somewhat less than the average for all New Mexico uranium ores. The deposit is mined by a large-scale open-pit operation. The initial discovery was made in 1951 by airborne radiometric survey, and subsequent drilling proved a moderate-sized deposit, now known as the South ore body. In 1953, a larger ore body, now called the North ore body, was found a short distance to the north; this body supplies almost all the current production from the mine.

The Jackpile and associated deposits are in the Jackpile sandstone. The North ore body, which is the largest, consists of at least two large tabular ore layers (Fig. 9). It is about 1,300 feet wide, several thousand feet long, and both layers total as much as 50 feet thick—probably averaging about 20 feet thick. It is elongated about N. 10° W. In addition a number of much smaller tabular deposits, as the Windwhip and the South ore body of the Jackpile mine, are satellitic to the North ore body.

The two ore layers of the North ore body are about midway between the top and bottom of the Jackpile sandstone. These layers lie essentially parallel to the major bedding of the sandstone (as shown in the longitudinal section, Fig. 9), though apparently they transect the bedding to some extent, as suggested in the cross section Figure 9, and certainly the top of the upper layer locally transects the crossbedding units, as shown in Figure 10. The crosscutting relations shown in Figure 10 are typical, though the upper boun-

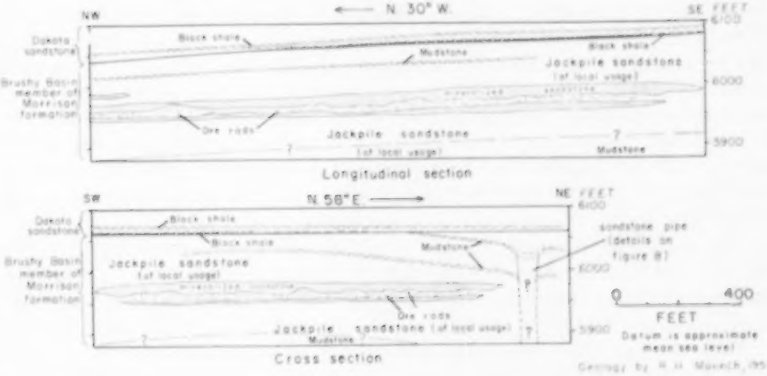


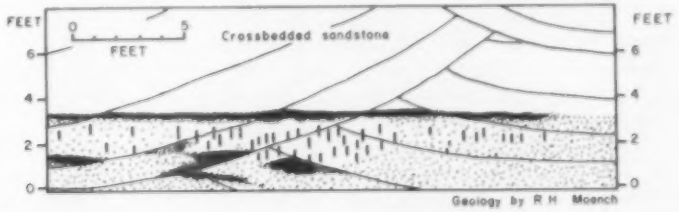
FIG. 9. Diagrammatic sections through the southern end of the North ore body, Jackpile mine.

dary of ore is not typically a flat surface, and locally the edge of ore follows bedding planes or thin discontinuous mudstone beds.

In contrast the grade variations within the deposit are strongly controlled by a multitude of sedimentary features. Clay galls, mudstone beds, and bedding planes commonly show concentrating effects, and large pods of high-grade ore commonly conform with trough cross-stratification. In addition, very sparse intraformational faults and joints show some concentrating effect.

In the mine area the Cretaceous rocks dip gently about N. 20° W., with local flattening and steepening, and the North ore body apparently conforms with the structural dip.

The long dimension of the North ore body may parallel the axis of a pre-Dakota anticline. In the cross section, Figure 9, this anticline is defined by two mudstone beds within the Jackpile sandstone. The uppermost mudstone bed, in the vicinity of the sandstone pipe, rises a short distance towards



EXPLANATION

Ore rods

Mineralized sandstone

FIGURE 10 -- FIELD SKETCH SHOWING RELATION OF TOP OF JACKPILE URANIUM DEPOSIT TO CROSSBEDDING IN SANDSTONE

the center of the section, and is truncated by the base of the Dakota sandstone. The lower mudstone bed rises to a crest just west of the center of the deposit, and then falls a short distance and pinches out on the west flank of the anticline. For lack of sufficient exposure the breadth, amplitude, and trend of the anticline are not known. Other folds nearby, however, are well exposed and trend N. 10° W. As this is a persistent regional trend of one set of pre-Dakota folds, it is likely that the fold exposed in the Jackpile mine also trends N. 10° W. and coextends with the long dimensions of the North ore body.

An extremely irregular complex diabase sill cuts much of the Jackpile deposit. This sill is related to the diabase dikes and sills of late Tertiary age that are abundant throughout the Laguna district. It averages several feet

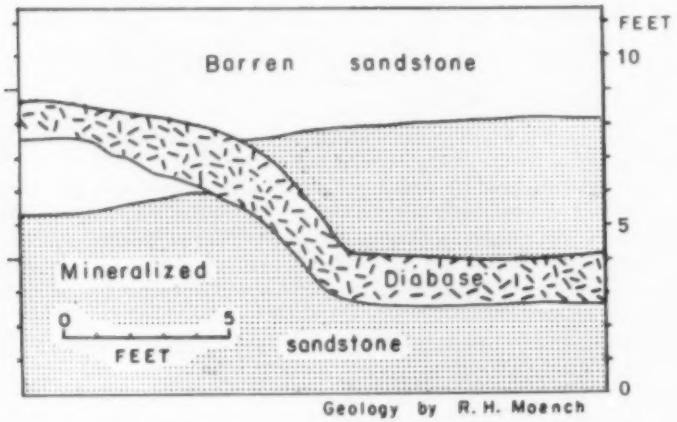


FIG. 11. Field sketch showing displacement of Jackpile uranium deposit by diabase sill.

thick and is essentially horizontal, but cuts randomly through the deposit—locally rising well above or falling well below it. In Figure 11 the sill is shown to cut through the top of the deposit. Here, the deposit is displaced by an amount equivalent to the thickness of the sill, indicating that the sill was emplaced later than the uranium deposit.

A sandstone pipe is exposed on the east side of the North ore body (Fig. 9). The top of this pipe is shown in Figure 8 and is described above in connection with sandstone pipes. Only the upper part of the pipe is exposed, the top of which is about 40 feet above the top of the ore body. Although organic materials are abundant within the pipe, they are absent in the wall rocks, and the pipe is essentially barren of uranium where exposed. Where it intersects the approximate level of the North ore body, however, it reportedly contains ore.

Vertical ore rods of uraniferous carbonaceous material constitute a unique and interesting feature of the deposit. Some of the rods are shown in Figure 12. They are vertical cylinders as much as 2 inches in diameter and 4 feet high, which tend to occupy the lower grade parts of the deposit (Fig. 10) and are especially abundant in the low-grade zone between the two main ore layers (Fig. 9). The bedding is undisturbed, although the rods cut across it, and many rods terminate at their tops or bottoms at bedding planes, whereas others feather out along the bedding. Very commonly the rods are zoned, consisting of a core of uraniferous carbonaceous material, bounded by a thin pyritic zone.

A number of relatively small uranium deposits have a distribution that is satellitic to the Jackpile deposit. These smaller deposits are similar to the Jackpile with respect to form, composition, and relation to the host sandstone. Two of the satellitic deposits are described briefly below.

The South ore body of the Jackpile mine is near the southwest corner of the North ore body. It has the same vertical position in the Jackpile sandstone, and likewise it consists of two main tabular ore layers. In plan it is oval, about 350 feet wide, 750 feet long, and as much as 50 feet thick. It is

FIG. 12. Photograph of vertical ore rods, Jackpile mine.

elongate about N. 70° E.—nearly at right angles to the elongation of the North ore body.

On the west side of the Jackpile deposit is the Windwhip deposit. Its horizontal dimensions are not known to the writers, but it is considerably smaller than the South ore body. The Windwhip deposit is in the Jackpile sandstone, but is stratigraphically higher than the Jackpile deposit. It is about 15 feet below the top of the Jackpile sandstone, and probably overlaps the western edge of the Jackpile deposit.

In the Windwhip deposit the general character and distribution of ore is illustrated in Figure 13. Here the ore conforms locally to the sedimentary structures, or transects such structures at a low angle. In many places, however, the ore has a smoothly curved edge that cuts sharply across the bedding. Such features are similar to the roll structures described by Fischer (4) and Shawe (15, 16) in other parts of the Colorado Plateau.

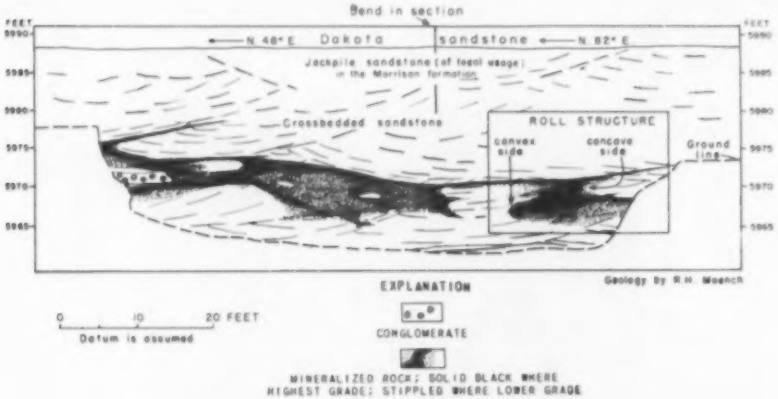


FIG. 13. Geologic wall map of the Windwhip deposit.

Poison Canyon and Associated Deposits

The Poison Canyon deposit is in the Ambrosia Lake district. It is one of the few large deposits in the district that is sufficiently developed to allow effective study. The general mineralogy and configuration of this deposit have been described by Dodd (2, 3.) Dodd's description, combined with the results of more recent work are summarized below. The deposit illustrates a more direct relation to sedimentary features than has been observed in deposits of the Laguna district.

The Poison Canyon deposit is in the Poison Canyon sandstone of the Morrison formation. It is a tabular deposit consisting of many sub-parallel layers. Individual layers are as much as 200 feet wide and 20 feet thick, and they form an aggregate as much as 700 feet wide and 35 feet thick. The

layers and the aggregate are all strongly elongated in an easterly direction. The deposit is near the base of the host sandstone, and concentrations are most abundant above or below thin mudstone beds. Dodd (2, 3) states that the deposit is elongate along the trend of sedimentary structures, and is localized in the central thick coarse-grained part of the unit. He indicates (2, Fig. 8) that the Poison Canyon deposit and also the Mesa Top deposit, immediately to the east of it, are in, and coextensive with, a "composite" channel in the Poison Canyon sandstone. Recent work bears out these relations, and subsurface information reveals that the "composite" channel extends eastward in a broad arc at least 7 miles long (Fig. 4). It is referred to here as the Poison Canyon trend.

The deposit is cut by a number of northward-trending faults, and all available evidence suggests that the faults are younger than the deposit. The ore layers are displaced by the same amount of throw as the units in the host rock. Dodd (2, 3) states that the grade and thickness of the ore increases adjacent to the faults, but also states that only secondary minerals are found on fault and fracture surfaces. More recent work has revealed that the higher grade concentrations adjacent to the faults are made up of minerals containing hexavalent uranium. The deposit is most oxidized near the faults, and it is probable that these concentrations formed by near-surface redistribution of uranium by ground water.

Uranium Deposits North of the Poison Canyon Deposit

North of the Poison Canyon deposit the uranium deposits of the Ambrosia Lake district constitute several multi-million-ton and numerous smaller deposits that account for more than one-half the total uranium reserves in the southern part of the San Juan Basin. Unfortunately they have not been developed sufficiently to study in detail. With respect to form, composition, and structural and stratigraphic relations, however, they are known to be similar to the other deposits in the Morrison formation. For lack of detailed information, the deposits of this area are described collectively.

As shown by their approximate outlines in Figure 4, the deposits in this area, the Ambrosia trend, constitute an elongate easterly-trending group that is essentially parallel to the Poison Canyon trend. The approximate vertical distribution of the deposits within the Morrison formation is shown in Figure 5. Individual deposits are essentially tabular and are within the host sandstones (Fig. 5) similar to the deposits in the Morrison and Entrada formations of the Laguna district. In general the deposits occur where the sandstones are coarsest and, locally, occur in one or more zones having an aggregate thickness of as much as 100 feet. In general, however, the deposits have average thicknesses that range from several feet to several tens of feet. They generally follow the bedding, but locally transect sedimentary units (see just right of the center of section C-C', Fig. 5) similar to that suggested for the Jackpile deposit.

Most of the deposits, including all those that contain more than about 1 million tons of material, are in the Westwater Canyon member; the others are

in the Brushy Basin member. As pointed out above in the section on stratigraphy, most of the deposits are near the central part of a thick mass of sandstone (Fig. 5), which is more extensive and uniform in an easterly direction than a northerly direction, except where it thins markedly over the Ambrosia dome.

The writers interpret that the belt of deposits in this part of the Ambrosia Lake district is coextensive with and controlled by the easterly trend of the thicker part of the sandstone mass. Absence of uranium deposits over the crest of the Ambrosia dome and the tendency to clustering of deposits around its periphery are probably related to the thinning of the host sandstone mass over the dome rather than to closure on the dome.

Woodrow Deposit

The Woodrow deposit, about 1 mile east of the Jackpile mine, is unique in the district, and probably on the Colorado Plateau. It is small, but high grade, the ore averaging nearly 2 percent uranium. It is particularly interesting, however, because it occupies a structure that may best be termed a sandstone pipe. The pipe (Fig. 14) is nearly vertical, has a known height of about 230 feet, and a maximum diameter of about 35 feet. It is bounded by a complex branching ring fault. The wall rocks include the Jackpile sandstone, and underlying beds of mudstone and sandstone. With the exception of probable downwarping and faulting in the near vicinity of the pipe, these rocks are essentially undeformed. The core of the pipe is made up of a heterogeneous mixture of sandstone and mudstone that appears to have been derived from the nearby wall rocks. Near the top of the pipe sandstone predominates; near the bottom mudstone predominates. The transition zone is about 35 feet below the base of the Jackpile sandstone, and probably indicates the amount of downward displacement of the core with respect to the wall rocks. Carbonaceous materials are abundant within the pipe, and a few fossil bone fragments have been found.

In the upper part of the pipe the ore is exceptionally high grade, and is concentrated mainly along the boundary ring fault. Here the core of the pipe is essentially barren, but the ore locally extends several feet outward into the Jackpile sandstone. In the lower part of the pipe the ore is much lower grade, though still higher grade than the district average, and is more or less homogeneously distributed throughout the core.

The ore concentration along the ring fault is a replacement, not a fissure filling. Massive sulfides, as pyrite and marcasite, commonly show relict bedding, in which the outlines of individual grains are visible. High-grade cofinite-sulfide mixtures locally show boxwork textures, controlled by bedding-fracture intersections.

As the top of the Woodrow pipe has been eroded and its bottom has not been found, its original stratigraphic range, age, and origin cannot be determined. The part of the pipe that is well exposed, however, is strikingly similar to the many hundreds of sandstone pipes that are exposed throughout the Laguna district (see previously). Although the Woodrow pipe is min-

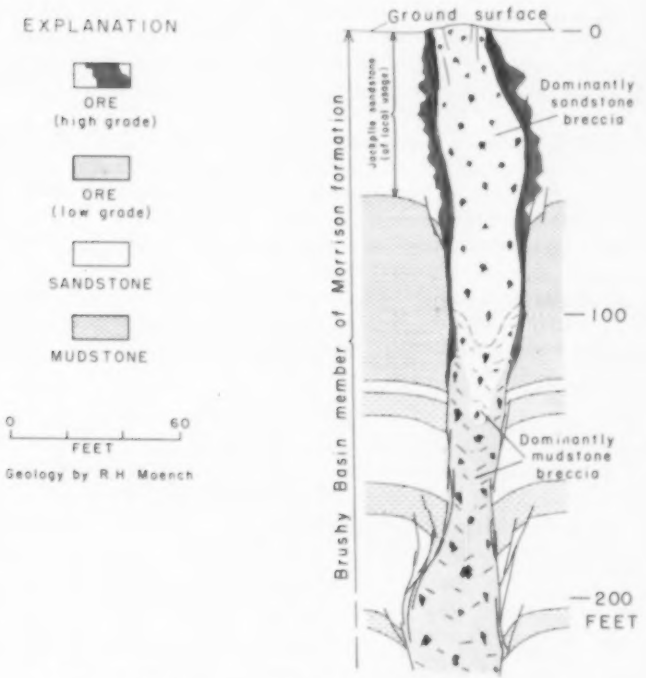


FIG. 14. Diagrammatic section through the Woodrow pipe.

eralized, the writers believe that it is the same type of structure as the others. If so, the ring fault acted as a locus of uranium deposition, rather than as a conduit.

Sandy Deposit

The Sandy deposit, which is in the Laguna district, is in an area about 2,000 feet wide by 4,000 feet long, referred to here as the Sandy mine area. This area contains many small deposits, including the Sandy, which occur in the Entrada sandstone and Todilto limestone. Little uranium ore has been produced from the area, but it is discussed to illustrate (1) the occurrence of uranium deposits in the Entrada sandstone and Todilto limestone, (2) the relation of deposits in the respective host rocks to one another and to a pre-Dakota monocline, and (3) the relation of the deposits to the diabasic sills and dikes.

The area is underlain by the Summerville formation, Todilto limestone, and Entrada sandstone. Thin diabase dikes of late Tertiary age and a great many diabase sills, as much as 75 feet thick, cut and have metamorphosed to some extent all of these rocks and many of the uranium deposits.

The dominant structure in the area is a monocline that is related to the major easterly trending set of pre-Dakota folds. The monocline trends easterly to northeasterly across the area. Its steep flank dips southward, is about 1,300 feet broad, and its maximum structural relief in the mine area is about 110 feet.

The Todilto limestone in the area contains a multitude of intraformational folds. These are small but pronounced structures, with amplitudes about equal to their breadths. The largest folds have a breadth of about 20 feet, and involve the entire thickness of limestone. The smallest are less than half an inch broad and commonly have a drag relation to the larger folds. In sections the folds have a variety of shapes, the most common of which is that of an asymmetric fan. The axes of the intraformational folds on the flanks and near the anticlinal bend of the monocline mostly parallel the larger structure, but near the synclinal bend they are highly sinuous and are not systematically oriented.

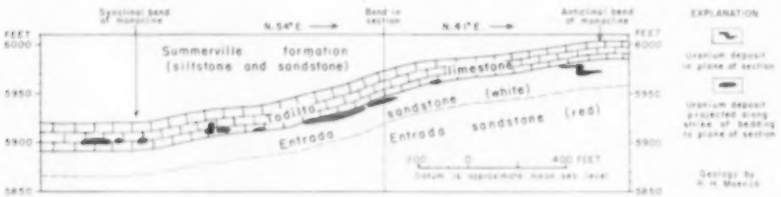


FIG. 15. Diagrammatic geologic section across Sandy mine area, showing transection of group of uranium deposits across monocline and base of Todilto limestone; diabase and intraformational folds deleted.

The known uranium deposits of the area constitute a group of deposits that are confined to the steep flank and anticlinal and synclinal beds of the monocline. Figure 15 illustrates the relation of the group of deposits to the monocline and to the two host rocks. To better illustrate these relations the diabasic dikes and sills have been removed from the section, and the structure restored to its prediabase position. This was done because the diabase is younger than the uranium deposits and distorts the earlier structure. Near the anticlinal bend of the monocline most of the deposits are within the Entrada sandstone. A few very small deposits are on the formational boundary, but none is in the Todilto limestone. Near the synclinal bend the deposits are all within the stratigraphically higher Todilto limestone. Also, downdip some deposits pass from Entrada sandstone into Todilto limestone. The relief on the group of deposits, therefore, is less than the relief on the monocline, and the group transects the formational boundary.

Figure 16 illustrates the essential physical features of a typical deposit in the Entrada sandstone. The deposit is tabular—about twice as long as it is wide. It is enclosed within the host sandstone—not bounded by any visible sedimentary or structural feature. In addition it shows roll structures,

FIG. 16. Section through uranium deposit in Entrada sandstone, Sandy mine.

as do many of the small deposits in sandstone. The axes of these structures parallel the average strike of crossbedding.

The deposits in the Todilto limestone are almost wholly associated with intraformational limestone folds. The deposits, therefore, are stringlike and highly sinuous in plan. Figure 17 illustrates in section the distribution of uranium with respect to the central part of a limestone fold. The uranium deposit, as indicated by the one-tenth and higher milliroentgen isorads, is dominantly in the massive thick-bedded limestone, which is in the center and at the base of the fold. In section the form of the deposit is crudely that of a reversed L, and it is coextensive with the fold.

The deposit is separated into three parts by two diabasic sills, which are younger than the deposit. As the lower sill is about 20 feet thick, the lowermost part of the deposit is not shown in Figure 17. The upper sill cuts the

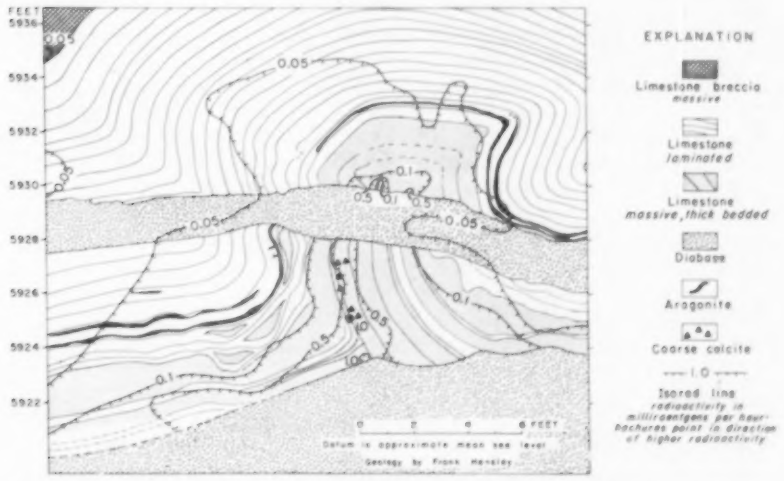


FIG. 17. Section across uranium deposit in Todilto limestone, Sandy mine area.

top of the deposit, and truncates all isorads higher than 0.05 milliroentgens. The 0.05 milliroentgen isorad reflects only an increase in general radioactivity toward the deposit. The highest grade parts of the deposit, and the major limestone units above the sill are all displaced to the right with respect to the same features below the sill. The lower sill cuts the base of the deposit. As this part of the deposit is the basal part of the reversed L, the higher grade isorads spread out beneath the base of the sill as well as immediately above the top.

F-33 Deposit

The F-33 deposit, in the Ambrosia Lake district (Fig. 2), is exposed in the workings of the F-33 mine and is an excellent example of a large uranium deposit in the Todilto limestone. It is discussed here to illustrate the distribution of the deposit with respect to the lithologic units in the limestone, and to minor folds.

The Todilto limestone at this mine contains the lower "platy," medial "crinkly" and upper "massive" units that persist throughout most of the region (see Stratigraphy). These rocks are strongly deformed, and they define a number of folds and faulted folds (Fig. 18). In contrast with much of the folding in the Todilto limestone the largest fold exposed in this mine involves the upper part of the Entrada sandstone. The best-developed fold in the F-33 mine is an anticline that has a width of more than 50 feet and a maximum height of about 7 feet. The northern flank of the anticline is steeper than the southern flank and is locally overturned and thrusted (Fig. 18). This

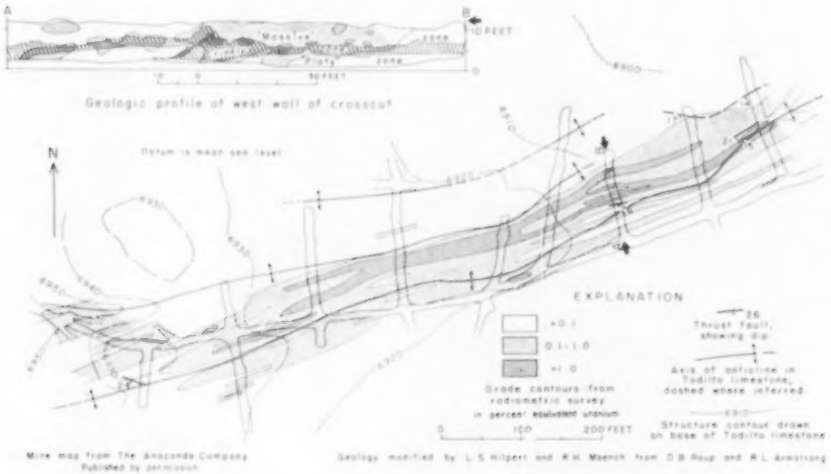

A
B
Massive
Crinkly
Platy
Entrada
Geologic profile of west wall of crosscut
N
Datum is mean sea level
EXPLANATION
Thrust fault, showing dip
Axis of anticline in Todilto limestone, dashed where inferred
Grade contours from radiometric survey in percent equivalent uranium
Structure contour drawn on base of Todilto limestone
Mine map from The Anaconda Company
Published by permission
Geology modified by L. S. Hilpert and R. H. Moench from D. B. Reup and R. L. Armstrong

FIG. 18. Generalized geologic map and transverse profile of part of the F-33 deposit.

structure, as well as the smaller linear structures exposed in the mine, is oriented about N. 70° E.

The uranium deposit is contained within all three units of the Todilto limestone (Fig. 18). Although most of the ore is in the "crinkly" and "massive" zones, there appears to be little direct relation between lithologic changes and distribution of the uranium deposit.

The deposit and the fold are closely coextensive. The deposit as a whole is about 100 feet wide, as much as 15 feet thick, and in excess of 1,200 feet long. Its long dimension, oriented about N. 70° E., is closely coextensive with the fold. Although the width of the deposit is much greater than the breadth of the anticline, its highest grade parts are mostly in the structural low just north of the steep or overturned flank (Fig. 18).

RESOURCES IN UNEXPLORED GROUND

The ore-bearing rocks between Gallup and Laguna dip northward, so, generally speaking, there is only one line of outcrop of these formations (Fig. 2). The known deposits have been found at this outcrop or, by subsurface exploration, at moderately shallow depths within a few miles north of this outcrop. It is possible that the pattern or frequency of distribution of these deposits at and near the outcrop continues in these formations northward under increasing depth of burial toward the center of the San Juan Basin; under these circumstances the undiscovered resources would be extremely large. On the basis of interpretations from known geologic relations, however, it seems more likely that the deposits will tend to be clustered in a zone at least 20 miles wide north of the present outcrop. Even though this concept of the southern San Juan Basin mineral belt restricts the favorable ground geographically, the amount of unexplored ground within the limits of this belt is enough to contain several times as much uranium resources as is now known. The geologic evidence and reasoning for this belt are reviewed below.

A short distance south of the Gallup-Laguna area the Morrison formation is cut out by the unconformity that underlies the Dakota sandstone. Although deposition of the Morrison undoubtedly extended to the south of this line, the existence of a broad area of nondeposition in central and southern New Mexico (13) suggests that the southern limit of deposition of the Morrison was not far south of its present southern limit (Fig. 1).

The Todilto limestone also pinches out in a depositional edge along a line a short distance south of Laguna and east of Gallup, and still farther south the Entrada is cut out by pre-Dakota erosion. The Gallup-Laguna area seems to have been close to the southern edge of the general basin of deposition in which the Jurassic rocks of the Colorado Plateau region accumulated. Perhaps the tectonic movements that during the Jurassic formed and sustained this basin caused the minor flexures in the Gallup-Laguna area. These flexures probably gave rise to the intraformational folds in the Todilto limestone, preparing the rock for later ore deposition; and these flexures may also have had some control on the positions and trends of the streams that formed the sandstone lenses, which are hosts for the deposits in the Morrison formation.

At any rate, because of these marginal relations, rocks favorable for ore deposits did not extend much farther south than the present line of outcrop between Gallup and Laguna.

Evidence to limit and predict the northern edge of this belt is even more tenuous, for the ore-bearing rocks are buried. Of course the pre-Dakota flexuring could have extended northward into the basin of Jurassic deposition, but it is more likely that this deformation was concentrated along, and perhaps restricted to, the basin margin. In the Laguna district the Jackpile sandstone thins northward from the Jackpile mine; and no significant uranium deposits are known more than a few miles north of the Jackpile mine. There has been little exploration north of the known deposits in the Ambrosia Lake and Gallup districts because of the increasing depth of burial of the ore-bearing rocks. There is some evidence, however, that the ore-bearing sandstones locally thin northward from the vicinity of the deposits in the Ambrosia Lake district. Where the sandstones show no apparent thinning they become more uniform in character. This greater uniformity of the sandstones suggests a depositional change basinward, possibly to quieter, or more uniform fluvial conditions, and the deposition of sediments that were probably unfavorable for the formation of significant uranium deposits.

In summary, the reasons for the existence of this belt of known uranium deposits are not fully known; the fact remains, however, that the belt parallels a number of controlling and definitive geologic features. In addition to the Jurassic highland and the southern limits of the Todilto limestone and the Morrison formation, it parallels the easterly trend of the major Jurassic folds, the dominant orientation of the intraformational folds in the Todilto limestone, the elongation of the thickest parts of the host sandstones of the Morrison formation, the dominant known sedimentary trends within these host sandstones, and, finally, it parallels the individual belts of deposits, as the Poison Canyon and Ambrosia trends.

SUMMARY AND CONCLUSIONS

Uranium deposits along the southern margin of the San Juan Basin occur in the Morrison, Todilto, and Entrada formations of Jurassic age and the Dakota sandstone of Cretaceous age. The known reserves have a total value of more than one billion dollars; most of these reserves are in the Morrison formation.

In the Morrison formation the ore minerals of the principal deposits are intimately mixed with a carbonaceous material that impregnates sandstone and forms tabular bodies that lie nearly parallel to the bedding. Most deposits are in the central part of thick sandstone lenses. Gentle folding during Jurassic time may have controlled the positions of the streams that formed these sandstone lenses.

The ore minerals in the Todilto limestone impregnate and replace the limestone where it has been deformed by intraformational folding and faulting. This deformation may have been caused by the flowage of unconsolidated lime muds on the flanks of the Jurassic flexures, for the intraformational

folds are localized along these flexures and many are elongate parallel to them. Typically the ore bodies in the Todilto are long but narrow.

Sandstone pipes are numerous in the eastern part of the area and also are localized along the flanks of these Jurassic flexures. Their position and their habit suggest that they resulted from some slumping action before consolidation of the beds they cut. Although only one of the several hundred pipes known has yielded uranium ore, and only one other reportedly contains ore, it is likely that these pipes provided loci for deposition of uranium, but were not channelways for ascending or descending uranium-bearing solutions.

Deformation during Jurassic time may have had some direct or indirect influence on the localization of the uranium deposits in the rocks of Jurassic age; there is no definite evidence that later tectonic structures had a genetic influence on the deposits. Although the genesis of the deposits is not known, it is believed that all of them had a common origin. It is suggested that solutions circulating through the rocks under water-table conditions could have formed deposits that would have habits like those in this area.

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U. S. GEOLOGICAL SURVEY,
SALT LAKE CITY, UTAH, AND DENVER, COLORADO,
July 20, 1959

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APPLICATION OF THE GRAVITY METHOD TO IRON ORE EXPLORATION

WILLIAM J. HINZE

ABSTRACT

The gravity method has played an increasingly important role in the search for new reserves of iron ores since the development of highly portable gravimeters capable of a high degree of precision. This method has been used in the search for and study of direct shipping ores, but it has proven to be especially useful in the study of large tonnage, wide, near surface "taconite type" ore bodies that have been the primary concern of the iron ore industry during the past decade.

The gravity method was first applied to iron ore exploration as a tool for detecting non-magnetic ores, but advantages of this method over other exploration methods have also made it useful under certain geological conditions in the study of magnetic ores and regional structures favorable for the occurrence of iron ore. However, the gravity method is restricted by several limitations that must be realized and understood if the application of the method is to be successful. In addition, the full utilization of the method is dependent on a complete understanding of the density relationships of ores and their contrast with the country rocks. This is made particularly difficult by the wide range of densities of iron ores that can lead to the association of both positive and negative gravity anomalies with iron ore bodies. The result is that the amount and quality of information interpreted from the results of gravity surveying is a direct function of the auxiliary geological information available either through geological or other geophysical studies.

INTRODUCTION

GEOPHYSICAL methods of exploration have played an increasingly important role in the search for new reserves of iron ore since the end of World War II. As the foreseeable demand for iron ore increased beyond the reserves of the established sources of supply and as improvements were made in geophysical instrumentation and technique, the established methods of iron ore prospecting with compass and dip needle have been supplemented with a variety of new ground magnetic instruments, airborne magnetic, gravity, electrical, electromagnetic, and seismic methods of exploration. The gravity method in particular has played an increasingly important part in iron ore exploration since the development of highly portable gravimeters capable of a high degree of precision.

The purpose of this paper is to review the application of the gravity method to iron ore prospecting, consider the advantages and disadvantages of the method and to show a few examples of the application of the method. The comments apply in general to iron ore prospecting and in particular to the study of Lake Superior type iron formations and ore bodies.

The term "taconite ores" used in this paper includes those ores that come under the legal definition of taconite in the laws of Minnesota as well as all low-grade iron-bearing rock that cannot be concentrated into ore by simple methods of crushing, screening, washing, jigging, or drying, but can be by magnetic, flotation, spiral, or electrical methods of concentration.

HISTORY OF THE APPLICATION OF THE GRAVITY METHOD

One of the earliest published reports on the use of gravity methods in iron ore exploration in North America is included in the report on geophysical studies at Steep Rock Lake, Ontario, by Dr. A. A. Brant in 1940 (4). Both a gravimeter and a torsion balance survey were conducted on the ice of Steep Rock Lake in the search for hematite ore bodies believed to exist below the lake. The gravimeter was used unsuccessfully because the motion of the lake ice prevented precision observations and the results of the torsion balance survey were complicated because of effects from the ledge topography beneath the lake sediments.

To the author's knowledge the first published test of the gravity method over a known iron ore body in the United States was reported by Barnes and Romberg in 1943 (2). They successfully used the gravity method to investigate quantitatively the Iron Mountain magnetite deposit in Llano County, Texas. The first published test of the gravity method over a known iron formation and ore body in the Lake Superior region was reported by Zinner in 1949 (11). This investigation was conducted during 1944 in the Iron River district of the Lake Superior region for the U. S. Bureau of Mines. The purpose of the survey was to investigate the possible use of the gravity method in the detection of direct shipping iron ores. According to Zinner (11, p. 3) in this study "Gravity-meter surveys met with limited success permitting inferences relative to the strike of local sedimentary beds."

Immediately after World War II several organizations experimented with gravity methods in the study of both direct shipping and taconite type ores. The surveys conducted by private organizations remain unpublished, but Bacon and Wyble in 1952 (1) reported on both a detailed and regional survey in the Iron River–Crystal Falls, Michigan, area and Woollard and Hanson in 1954 (10) reported on surveys conducted by the University of Wisconsin in the Vermilion, Gogebic, and Baraboo iron ranges. These surveys met with varying degrees of success depending on local geological conditions.

APPLICATION OF THE GRAVITY METHOD

The gravity method has been applied to iron ore exploration (1) to aid in quantitative studies of both magnetic and non-magnetic ore bodies, (2) as a tool in the search for non-magnetic ores, and (3) as a reconnaissance tool in the study of regional structures that are favorable for the occurrence of iron ore. In many exploration organizations the principal application of the gravity method has been the quantitative study of ore bodies. The purpose of these studies include determining the areal and subsurface extent, the

attitude and structure, and the tenor of the ore body. The gravity method has been used primarily in conjunction with other geophysical methods and/or geological studies. The success of the method in quantitative studies, all other things being equal, is strongly dependent on the limitations imposed by the results of these other studies. This is true because the gravity method, like all other methods based on potential fields, does not uniquely define the geometry of the causative mass and the contrast of the physical property that is measured.

The gravity method has been used in the study of direct shipping ores, but it has proven to be especially useful in the study of taconite type ores, which have received the major interest of the iron ore industry during the past decade. To be of economic interest most taconite ores in addition to containing a certain minimum iron content must occur in wide ore bodies of large tonnage close enough to the surface to be mined by open pit methods. These factors—large tonnage, wide ore bodies, and surface proximity—make taconite ores particularly amenable to study by gravity methods. Most taconite ores also are not subject to the density fluctuations that can exist in direct shipping ores.

Basis of the Gravity Method.—The gravity method is based on measurements of small variations in the vertical acceleration of gravity. The difference between the observed variations and the theoretical values of gravity calculated from a knowledge of the gravitational field of the earth is called a gravity anomaly. The theoretical values of gravity used in the calculation of the Bouguer gravity anomaly, the type of anomaly employed in most geological interpretations, includes the effect of latitude, elevation and included mass above or below a datum, and local terrain departures. The anomaly values indicate any departures from the mass distribution assumed in calculating the anomaly. Horizontal variations in density causing these departures are the origin of the gravity anomaly. Vertical variations in density of horizontal layers affect all observations to the same degree and, therefore, will not affect the anomaly.

The density contrasts of particular interest in gravity prospecting for iron ore are the variations between the iron formations or ores and the country rock or the contrast between formations that have a structural or stratigraphic relationship to the occurrence of iron formations or ores.

Density Relationships.—Positive gravity anomalies are normally found associated with iron ores due to the positive density differential between the ores and the country rocks. The positive differential reflects the greater density of the iron minerals as compared to the minerals making up the major portion of the country rocks. The major iron ore minerals—magnetite and hematite—have densities of around 5.1, and the minerals of the country rock commonly range in density from about 2.6 to 3.0. The contrasts found in nature are seldom as great as suggested by these densities because the ores contain impurities, principally silica either in the form of quartz (chert) or combined with iron or other cations to form silicates, which lower the densities of the ores.

The density of an ore depends on the included minerals and their relative proportions. Figure 1 illustrates the theoretical relationship between density and per cent iron in a magnetite-quartz rock and in a hermatite-quartz rock, both of which are commonly approximated in nature. These relationships are useful as first approximations in the analysis of gravity data, however,

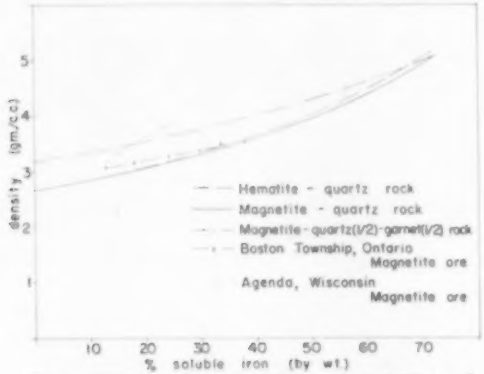

Fig. 1 Relationship between density and percentage of soluble iron for theoretical and observed iron ores.

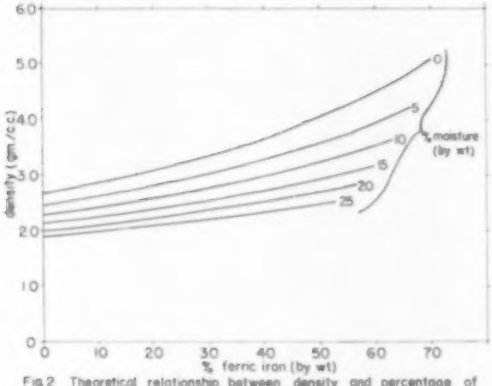

Fig. 2 Theoretical relationship between density and percentage of ferric iron in a hematite-quartz formation with varying degrees of porosity.

their use can lead to serious errors if ores are highly porous or contain significant proportions of minerals other than quartz, particularly the high-density anamorphic minerals.

Garnet is one of the anamorphic minerals that occurs in high enough proportion in some ores to have an effect on the density-percent iron relationship. A theoretical example of garnet's effect on the density of a magnetite-

quartz rock is shown in Figure 1. Garnet (assumed density—4.0) and quartz (assumed density—2.65) are assumed to make up equal proportions of the gangue by weight. It is obvious on comparison of this curve with that of the simple magnetite-quartz rock that the presence of garnet causes serious variations in the density-percent iron relationship. It is significant to note that the slope of the curve for the magnetite-quartz-garnet rock is less than that for magnetite-quartz rock indicating that the distinction between rocks of varying iron content is more difficult when garnet is present in the gangue. Also shown in Figure 1 is the line that best fits the trend of 52 density determinations of the Boston Township, Ontario, magnetic taconite ore varying in content from 13 to 37 per cent soluble iron as determined by the method of "least squares." This ore consists of magnetite and quartz with garnet quite common in some sections. Possibly the presence of garnet is reflected in the figure by densities greater than the theoretical magnetite-quartz relationship over most of the investigated range.

The effect of grunerite, which is another common gangue mineral in some possible taconite ores, on the densities of iron ores is shown in Figure 1 by the "least squares" line for 6 samples totaling 43 kg of the Agenda, Wisconsin, taconite ores. Certain horizons of this magnetite formation are rich in iron silicates, particularly grunerite. Graphite and iron sulfides also occur as minor impurities. The samples tested, ranging in soluble iron content from 15 to 25 percent, were found to vary in density from 0.4 to 0.7 above the normal densities of a simple magnetite-quartz rock.

Although positive density differentials and gravity anomalies are generally associated with iron formations and ores, negative differentials and anomalies can exist, thus providing distinctive and often important relationships. Negative gravity anomalies may occur in association with taconite ores when the density of the country rock exceeds that of the iron-rich rocks. An example of this situation is found in the Vermilion iron range of Minnesota where the Soudan iron formation occurs interbedded with the Ely greenstone. This iron formation as studied at the eastern end of the district on the Fortier-Mills property consists of magnetite, quartz, and locally iron silicates. The density of the magnetite-rich iron formation is 3.20 whereas the magnetite-lean iron formation has a density of only 2.80. These densities are in contrast to the greenstone, which has a mean density of 2.95. Thus the economically interesting iron formation has a positive density differential with the greenstone, whereas the lean iron formation has a negative differential. Although negative anomalies associated with the lean iron formation have no direct economic interest they are of aid in tracing the strike of the iron formation and determining the regional structure.

Negative gravity anomalies may also be associated with direct shipping ores. Brant (5) reports on such an association in the Labrador trough area. The process of iron concentration from an iron-silica formation by the oxidation of iron and the leaching of silica leads to an increase in porosity and therefore to a decrease in density. The result is a negative density differential between the iron ore and iron formation or country rocks and thus

a negative gravity anomaly. The theoretical relationship of density versus percent iron by weight in a hematite-quartz formation with varying degrees of porosity is shown by the family of curves in Figure 2. The porosity is indicated by the percent moisture by weight since all the pore spaces are assumed to be water filled. Although there are inherent dangers in using these curves because of the assumed simplified mineralogy, they can be very useful for approximations and as guides to relations from rocks of more complex mineralogy.

These curves suggest that direct shipping ore containing above 50 percent by weight ferric iron occurring in an iron formation that contains 20 percent ferric iron by weight with no porosity may have the same, a smaller, or a greater density (3.1) than the iron formation. The sign and magnitude of the density contrast depends on the porosity of the iron ore. The significant point is that a direct shipping ore body lying within an uneconomical iron formation may under certain porosity conditions give rise to no gravity anomaly or even a negative anomaly. The successful detection of such ore bodies by gravity methods is very difficult except where geological data sufficiently limits the possibilities. Further complicating this situation is slumpage and compaction of the ore, a common phenomenon, with consequent decrease in volume and pore space of the ore and thus an increase in density. Therefore, it is possible for the vertical variation of the density contrast in an ore body to vary from positive at the bottom due to compaction to negative at the top where there is limited compaction. This possibility greatly complicates gravity interpretation, but with proper background geological information interpretation is still feasible.

The decrease in volume of the ore from slumpage may also indirectly lead to negative gravity anomalies associated with ore bodies if the slump reaches through to ledge causing ledge caving. Caving at ledge causes a depression, which when filled with overburden will give rise to a negative density differential between the overburden and the ledge rock and thus a negative gravity anomaly over the sub-outcrop of the ore body. Zinner (11, p. 27–28) reports on an anomaly in the DeGrasse area of the Iron River district that possibly has this origin.

Advantages of the Gravity Method.—The gravity method has been applied to iron ore exploration because of its inherent advantages and because of weaknesses in other iron ore exploration techniques, and also to corroborate the more universally applied magnetic method. A discussion of some of the more important advantages and applications of the gravity method to iron ore prospecting follows:

(1) The gravity method was first applied to iron ore exploration as a tool for detecting the presence of non-magnetic ores. Gravity methods are applicable to this type of exploration because density is one of the few physical characteristics and in many cases the only characteristic of hidden non-magnetic ores that is distinctive and can be detected by present geophysical methods. However, as pointed out previously, the densities of these ores are not universally distinctive.

Gravity surveys for non-magnetic ores are usually conducted in limited areas suggested for study by geological data and/or magnetic anomalies originating from magnetite associated with the non-magnetic iron ore minerals. Regional gravity surveys for non-magnetic iron ores are normally not feasible on the same basis as regional magnetic surveys because the density contrasts involved do not necessarily give rise to sufficiently diagnostic gravity anomalies.

Non-magnetic concentrating ores occasionally occur in sufficient quantities associated with magnetic taconite ores to be economically interesting. The presence and distribution of these ores can best be studied with the gravity method. This method can also be useful in tracing out magnetic iron ores that grade into non-magnetic iron formations.

(2) Although it is undoubtedly true that magnetic methods of exploration are most applicable to the detection of magnetic iron ore, and even to the detection of non-magnetic ores containing minor quantities of magnetic ore minerals, the gravity method can be extremely useful and in some cases more useful than the magnetic method in the quantitative study of these ores. This point has been emphasized by Chapman (6) in his geophysical study of two magnetic taconite ore bodies. Quantitative studies of the physical parameters of an ore body—dimensions, geometry, and iron content—are under some geological conditions more aptly made from the results of a gravity survey than from a magnetic survey because:

(a) The magnetic effects from a body originate from two poles of opposite sign. The superposition of effects from these poles, attractive as well as repulsive, complicates magnetic interpretation and lowers the accuracy of quantitative analysis. Quantitative gravity analysis does not suffer from this defect since the gravity force field originates from the mass particles of the body, all of which have the same sign.

(b) The major iron ore minerals, hematite and magnetite, have specific densities, thus densities of their ores containing the common gangue minerals are a direct function of their content. Porosity is the major factor complicating this neat relation, but porosity is only important in some direct shipping ores, in ores where carbonates have been leached and in taconite ores where magnetite has undergone oxidation. Generally, however, taconite ores have negligible pore space. The direct function between density and quantity of iron ore minerals is in contrast to the relation between magnetic susceptibility, the source of magnetic variations, and the quantity of magnetic minerals present. This relationship is complicated by the environmental history, grain size, grain shape, and distribution of the magnetic minerals. Since these factors are both difficult to determine and evaluate, quantitative analysis from magnetic studies is usually tainted with a marked degree of uncertainty.

(c) Gravity studies give a better picture of the entire anomalous body than do magnetic studies. This is true because magnetic anomalies emphasize the near surface anomalous material more than gravity anomalies. This fact, which has been observed from the comparison of drilling results with the magnetic and gravity anomalies over iron formations, is illustrated in Figure

3. This figure shows the distance relationship for both gravity and magnetics as a function of the horizontal distance from a point over the center of a thin vertical sheet, a form commonly approximated by iron ore bodies. The relations based on calculations assuming a vertical magnetic field are shown for the entire anomalous body and also for both the upper and lower halves of the body. It is evident from these relations that the top half of the anomalous body contributes more to the magnetic anomaly than it does to the gravity anomaly. Over the midpoint the ratio of the effect of the top half

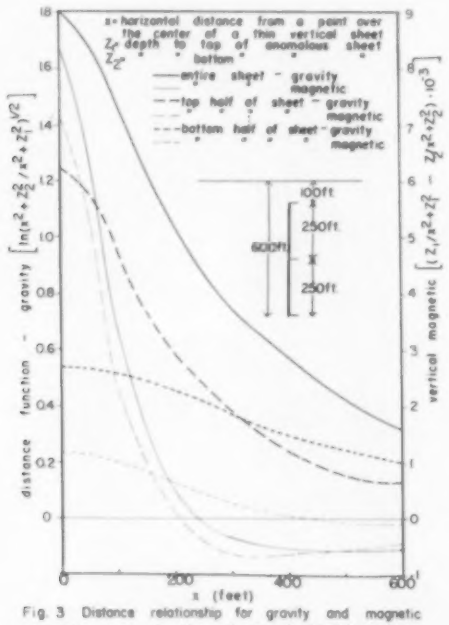
x = horizontal distance from a point over the center of a thin vertical sheet
Z_T depth to top of anomalous sheet
Z_B " " bottom " "
entire sheet - gravity
" " - magnetic
top half of sheet - gravity
" " " - magnetic
bottom half of sheet - gravity
" " " - magnetic
100ft
250ft
600ft
250ft
distance function - gravity $\left[\ln(x^2+Z_B^2/x^2+Z_T^2)^{1/2}\right]$
vertical magnetic $\left[(Z_T/x^2+Z_T^2) - Z_B/x^2+Z_B^2)\cdot 10^3\right]$
x (feet)

Fig. 3 Distance relationship for gravity and magnetic anomalies as a function of the horizontal distance from a point over the center of a thin vertical sheet in a vertical magnetic field.

to that of the entire body is 0.70 for gravity compared to 0.86 for magnetics and at a horizontal distance of 100 feet from the midpoint the ratio is 0.65 for gravity and 0.70 for magnetics.

A more general case is illustrated in Figure 4. In this figure the relationship is given for the distance function of both gravity and magnetic anomalies over the midpoint of a two-dimensional (i.e., infinitely long), rectangular, vertical sheet as a function of the depth of the bottom of the sheet when the depth to the top of the sheet and the thickness are held constant. The distance function for the gravity value over the midpoint of a vertical sheet

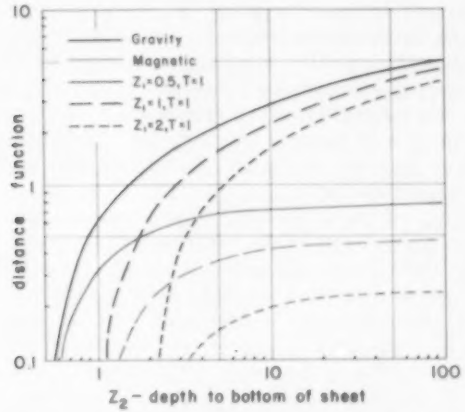

Fig. 4 Relationship between the distance function of gravity and vertical magnetic anomalies over the midpoint of a vertical sheet as a function of the depth to the bottom of the sheet when the depth to the top and thickness are held constant.

as derived from the general equation for the gravity effect over the midpoint of a vertical sheet

$$g = 2\gamma\sigma\left[\frac{t}{2}\ln\left(\frac{r_2 r_4}{r_1 r_3}\right) + 2Z_2\tan^{-1}\frac{t}{2Z_2} - 2Z_1\tan^{-1}\frac{t}{2Z_1}\right]$$

where g = gravity anomaly, γ = gravitational constant, σ = density contrast, t, Z_1, Z_2, r_1, r_2, r_3, r_4 are shown in Figure 5, can be reduced to

$$f_1(Z) = \frac{t}{2}\ln\left(\frac{t^2 + 4Z_2^2}{t^2 + 4Z_1^2}\right) + 2Z_2\tan^{-1}\frac{t}{2Z_2} - 2Z_1\tan^{-1}\frac{t}{2Z_1}.$$

The distance function for the magnetic value over the midpoint may similarly be reduced from the general equation for the magnetic effect of a vertical sheet striking magnetic north

$$V = 2kV_0(\phi_1 - \phi_2 - \phi_3 + \phi_4)$$

where V = vertical magnetic anomaly, k = susceptibility contrast, V_0 = earth's normal vertical magnetic field, ϕ_1, ϕ_2, ϕ_3, ϕ_4 are shown in Figure 5, to

$$f_2(Z) = \tan^{-1}\frac{2Z_2}{t} - \tan^{-1}\frac{2Z_1}{t}.$$

The relationships in Figure 4 show that the depth to the bottom of the vertical sheet does not affect the distance function for magnetics as greatly as it does for gravity. This is particularly true for depths to the bottom

of the sheet that are 10 times or more the depth to the top of the sheet. Beyond this depth the distance function for magnetics remains relatively constant. As Z_2 approaches infinity the distance function for magnetics asymptotically approaches a value of 1.5708—$\tan^{-1}\ 2Z_1/t$; this is in contrast to the distance function for gravity, which approaches infinity. The insensitivity of the distance function of magnetics to variations in the depth to the bottom of a vertical sheet seriously limits the quantitative information that can be extracted from magnetic anomalies.

The insensitivity of the magnetic method, however, can be used to advantage when properly appreciated. An example of this is the analysis of the direction of dip of a steeply dipping, magnetic sheet. The direction of dip is often difficult to determine when the angle of dip is very high and, as often is the case, when the sheet is magnetically hetrogeneous, however, the direction of dip even though it is only a few degrees off the vertical can be very important in selecting drilling sites. Magnetics when used with gravity studies can give a clue to the direction of dip. The gravity anomaly will be shifted from the magnetic anomaly in the direction of the dipping formation since the gravity anomaly is affected by the entire formation and the magnetic anomaly by only the anomalous material near ledge. Under some circumstances it is necessary to correct for the shift of the magnetic anomaly due to the inclination of the earth's field before the comparison can be made.

(d) The total mass of the anomalous formation can be calculated from the gravity anomaly as shown by Hammer (*7*). This can be very useful in

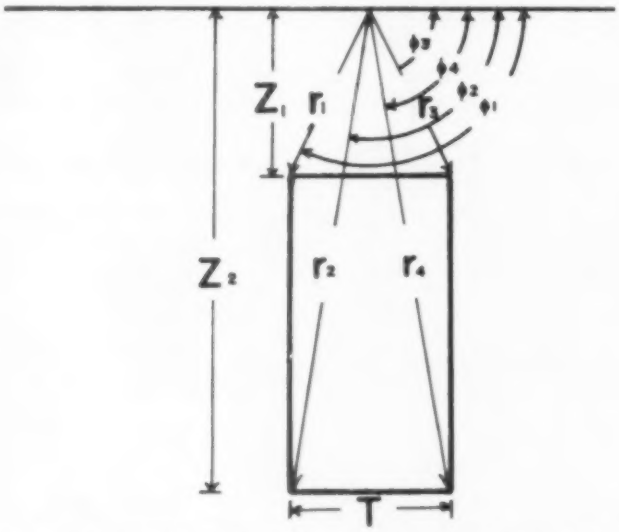

FIG. 5. Definition of variables used in calculating gravity and magnetic effects from a vertical sheet.

the study of direct shipping ores to be mined underground. However, it is of limited value in the study of taconite ores that are to be mined by open-pit methods, since the tonnage calculated is that of the entire anomalous mass and economic considerations limit the depth of mining and seldom permit mining the entire body.

(3) Magnetic anomalies are subject to displacement from the axis of the magnetic formation. This can cause difficulty in interpretation since the factors on which the amount of shift depends, the parameters of the earth's normal field and the geometry of the anomalous body, are difficult to evaluate. The displacement effect is particularly important in studies carried out at low magnetic latitudes or in studies of deeply buried formations. Gravity studies are not complicated by this effect.

(4) Density, the physical property on which gravity studies depend, is easier to measure and measurement requires less elaborate apparatus than magnetic susceptibility measurements. Also, generally speaking, density values are less susceptible to variations than magnetic susceptibility values, thus requiring fewer measurements.

(5) Gravity studies are less affected by man made disturbances than are magnetic studies. In particular gravity observations are unaffected by power lines, fences, iron and steel refuse, etc., which greatly complicate magnetic observations.

Disadvantages of the Gravity Method.—Although the gravity method is an important tool in iron ore exploration, it does suffer from several limitations that must be realized and understood if the application of the method is to be successful. Most of the disadvantages discussed below are inherent in the method and as such apply to the general application of gravity to mining geophysics, though the emphasis is different for each application.

(1) The anomalous property used in the gravity study of magnetic iron ores is less diagnostic than the anomalous property used in the magnetic study of these ores. The density of iron ores seldom exceeds a value of one and one-half times the density of the country rock, however, the magnetic susceptibility of iron ores is often 25 times or more the susceptibility of the country rocks. This is one of the main reasons why the gravity method cannot rank with the magnetic method as a tool for the detection of magnetic ores.

This too is a factor to consider in quantitative analysis of anomalies. In the case of magnetic interpretation, it is usually safe to assume that the country rock carries a negligible quantity of magnetic minerals, but in gravity interpretation it is of course necessary to establish the density of the country rock to determine the density differential. The correct estimation of the density of the country rock is one of the principle limitations of quantitative gravity analysis. Estimating the density of the country rock is difficult because the rocks enclosing iron ores and formations have a wide range of densities and generally are less well known. They are less well known because core drilling for the purpose of delineating and sampling the iron-rich rocks is planned to penetrate the minimum amount of country rock. Seldom can expensive core drilling of the country rock be justified for the single pur-

pose of obtaining samples for density measurements especially since it requires extensive drilling to obtain a representative sample. Outcrops of the country rock from which samples may be obtained are generally rare too. This is especially true in the investigation of taconite ores because if outcrops are present they consist mainly of the more resistant iron ores and formations. As a result the density of the country rock is usually estimated on limited knowledge. However, auxiliary geophysical information can be used to aid in identifying the country rock and thus limit the possible range of densities.

(2) The gravity method is incapable of detecting beds or masses of waste material in iron ores that do not have a density contrast with the ore. This situation is common in taconite ores that are adulterated with silicate horizons, or basic dikes, which may have little or no density contrast with the iron ore, but may have sufficient magnetic contrast to be detected by magnetic methods.

(3) An invalid assumption often made in the interpretation of gravity results in iron ore exploration is that the ledge surface is a horizontal plane. Although the iron ores of the Lake Superior region occur in terranes that have undergone peneplanation, there still exists enough relief in the ledge surface of these areas to cause false anomalies that distort and confuse the geologically interesting anomalies. The effect of bedrock relief is particularly important because the density contrast between the overburden and ledge rock exceeds that of most contrasts found in Precambrian terranes. The problem is particularly perplexing since the major bedrock relief is commonly controlled by lithology, thus the variations in lithology and ledge relief are superimposed on each other.

The effect of ledge topography is illustrated in Figure 6. The assumption made in this figure is that the top of a thin vertical iron formation containing 20 percent magnetite by volume lies 50 feet above the general level of the country rock, which is covered with 200 feet of overburden. The resulting gravity anomaly is 1.5 times the magnitude of the anomaly if the top of the iron formation is level with the country rock. Ledge relief also has a major effect on magnetic anomalies as indicated in the illustration.

The effect of ledge relief is dependent not only on the magnitude of the relief, but also on the overall depth of the ledge rock. For example, the effect of a horizontal slab of rock of infinite strike length that is 200 feet wide and 20 feet thick superimposed on a ledge surface of a depth of 30 feet will be 3 times that if the same slab were superimposed on a ledge surface of a depth of 200 feet.

(4) A common source of error in gravity surveys is the use of a wrong combined elevation correction factor (combined free-air and Bouguer corrections) based upon an improper selection of the representative density of the material between the reference elevation and the individual stations. The error that shows up in the magnitude of the anomalies, depends on the amount of topographic relief involved since the correction factor is multiplied by the elevation of the individual stations above or below the reference eleva-

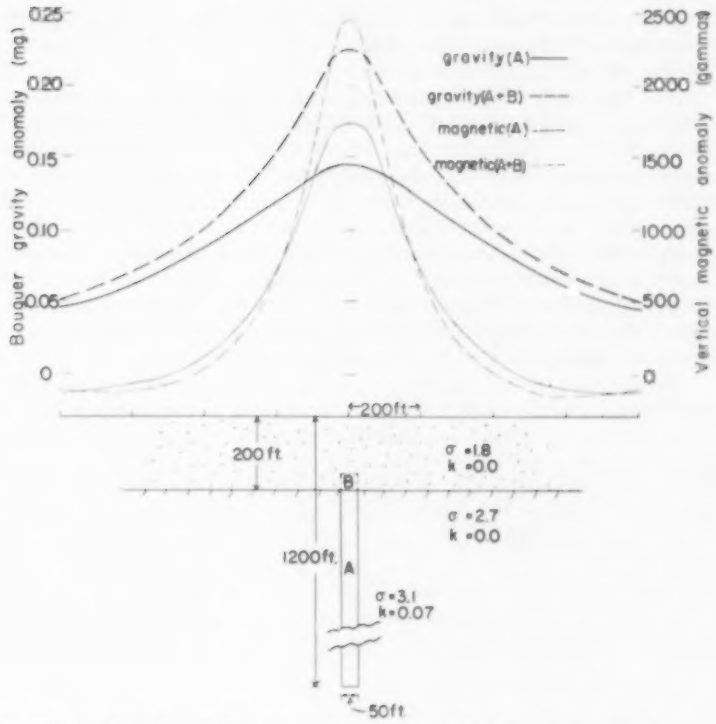

Fig. 6 Effect of ledge relief on gravity and vertical magnetic anomalies.

tion. The sign of the anomaly error is a function of the sign of the error in density and also the sign of the elevation with respect to the reference datum. The possible alternatives are shown in Figure 7. The magnitude of the error is 0.00128 mg/ft for each 0.1 g/cc error in density, thus it can have serious effects on the interpretation of gravity anomalies.

(5) In the calculation of Bouguer gravity anomalies an assumption is made that the station is located on a horizontal slab of infinite extent. This assumption is invalid in areas of rugged surface relief and thus terrain corrections are necessary. An example of error due to terrain effects is illustrated in Figure 7. The corrections are laborious to calculate and require good topographic maps of the local area, which often are not available. However, this correction is negligible in many areas containing Precambrian iron ores due to the surface levelling action of the Pleistocene glaciation. Where corrections are necessary they often can be approximated by Hubbert's (9) curves, which assume that the topographic features are of infinite length and constant cross section. These assumptions are commonly valid within

the limits of error of the method. Nevertheless detailed corrections are often necessary for studies conducted near existing mines because of the presence of dumps, stockpiles, open pits, or caves.

(6) The most serious problem in the analysis of gravity data in many areas is the correct elimination of the regional gravity anomaly. The regional anomaly, which originates primarily in regional structures and deep seated geological features, but which also may include the effect of ledge surface relief and cumulative errors, often obscures the economically interesting anomalies to a degree where it highly distorts them or even completely masks them. The regional anomalies associated with some sedimentary Precambrian iron formations in the Lake Superior region are particularly distorting where the vertical formations lie near the contact of two large rock units of dissimilar density. A typical example is cited in the example at the end of the paper and is illustrated in Figure 10.

The problem of the regional anomaly is not only one of eliminating it, but also of obtaining enough information about it so that it can be eliminated. This calls for extending the surveys beyond the limits of the economically interesting areas with resultant increase in the cost of the gravity surveying. In addition, extending the surveys is often impossible because of physical features or ownership problems that reduces the effectiveness of the surveys.

(7) An inherent disadvantage of the gravity method is that gravity anomalies are broader and thus less definitive than magnetic anomalies originating from the same anomalous body. As pointed out in discussing the advantages of the gravity method (2c), the magnetic method emphasizes the near surface anomalous material more than the gravity method and is

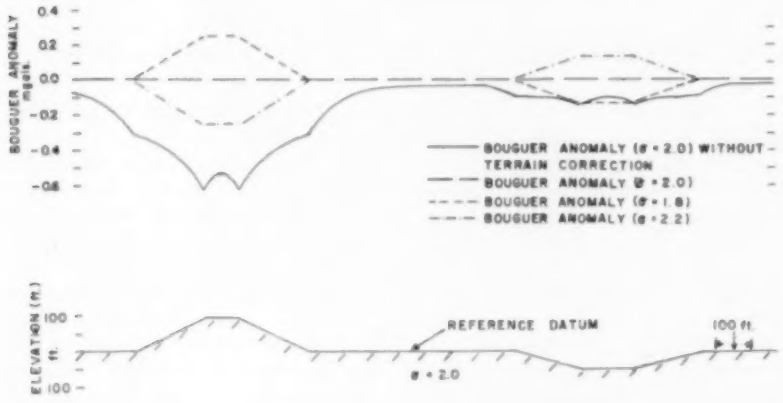

Fig. 7 Effect of surface relief (assuming two dimensional topographic features) and combined elevation correction factor on the Bouguer gravity anomaly.

little affected by the contribution of the material at a depth of 10 times or more the depth to the top of the body, as a result magnetic anomalies are sharper than the gravity anomalies from the same body (Fig. 3). This factor is particularly important when two or more anomalous bodies occur near enough together that their anomalies overlap, a situation commonly found in iron ore exploration.

(8) Experience has shown that gravity surveys are from two to three times more expensive than magnetic surveys. There are many reasons for this, but the main one is that relative elevations of all gravity stations must be determined to an accuracy of a tenth of a foot. This not only requires extra time, equipment, and men, but requires "brushed" lines along which the elevations may be carried. Cutting lines can be expensive in heavily wooded or "bush" country. In addition, the initial investment and unkeep is greater for gravity equipment than for magnetic gear, and gravity computations are extremely time consuming.

TYPICAL EXAMPLES

A few typical examples of the application of the gravity method to iron ore prospecting are given to illustrate the use of the method and to show some of the types of anomalies encountered. The examples are concerned primarily with taconite type ores and are all from properties within the Lake Superior region. The examples are not presented to cover comprehensively the complete geophysical studies of the properties, but rather to illustrate the use of the gravity method. It is hoped that in the future the complete geophysical case history of some of the properties will be presented.

Example I. The Jones & Laughlin Steel Corporation made a geophysical study of the Fortier-Mills property in the Vermilion range, Minnesota, to locate and delineate the structure of the Keewatin iron formation known to occur in the area from outcrop data. After the economically most interesting areas were located with a ground magnetic survey and preliminary core drilling was completed a limited gravity survey was conducted to aid in evaluating the property.

Geologically this area consists of steeply dipping greenstones with interbedded iron formations. The iron formations contain magnetite, quartz, and locally iron silicates. The thickness of the glacial overburden varies from zero to perhaps 50 feet. The average thickness is probably 10 to 15 feet.

A density study of a suite of drill cores selected from the area indicates that the density of the greenstone (2.95) is intermediate between that of the magnetite-lean iron formation (2.80) and the magnetite-rich iron formation (3.20). The magnetite-rich formation contains around 25 percent crude iron by weight whereas the lean iron formation carries 10 percent or less.

The gravity investigation provided information about the local and regional structure and in addition indicated that no large magnetite-rich formations exist at depth that were not encountered in the core drilling. The discrepancy between the high magnetic anomalies and the associated poor grades of magnetite ore that was found in the drilling suggested that the drilling did

not intersect all of the principal iron-rich formations, possibly due to pinching out of the greenstones. However, the gravity information indicated that this was not the case.

A typical section at right angles to the strike of the anomalous formations is shown in Figure 8. The vertical magnetic intensity anomaly is included with the results of the core drilling and the Bouguer gravity anomaly profile to facilitate comparison. The two main groups of iron formation centered at 500E and 1100E are both indicated by the gravity. The magnetic anomaly centered at 1100E is only slightly less prominent than the other main magnetic anomaly, which is in contrast to the significant difference in the corresponding gravity anomalies. This suggests that the iron formation at 1100E decreases in magnetite content with depth and/or does not extend as deeply as the iron formation centered at 500E.

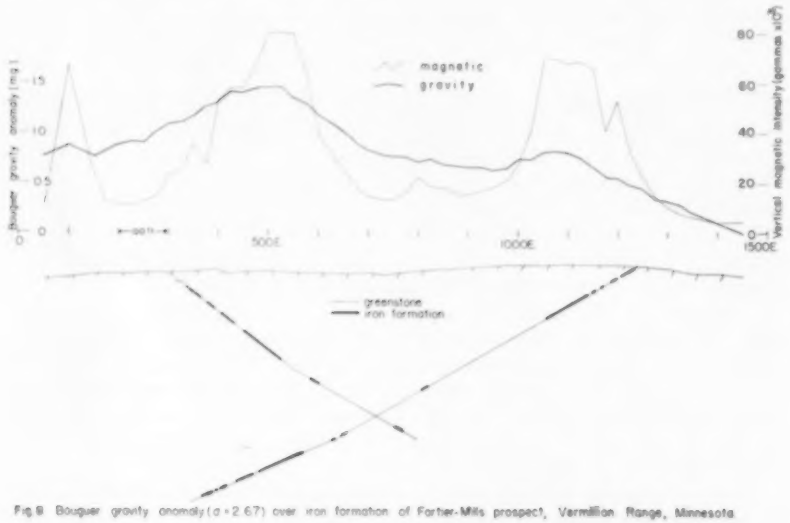

Fig. 8 Bouguer gravity anomaly ($\sigma = 2.67$) over iron formation of Fortier-Mills prospect, Vermilion Range, Minnesota

Example II.—The Magnetic Center iron formation located in Iron County, Wisconsin, has been described generally by Beutner (3). The iron formation, which has a maximum stratigraphic thickness of over 1000 feet, dips approximately 65° to the south and is bounded on the footwall and hanging wall sides by chlorite schists. The iron formation appears to be a thickened lens of iron rich rocks in the schists of the Marenisco Range. The prospect does not outcrop and drilling and seismic refraction studies indicate the glacial overburden averages about 70 feet thick.

Since there are no outcrops of the iron formation, the location of the deposit and guiding of the core drilling has been a geophysical problem. Magnetic surveys originally located the prospect and have played the major role

in delineating the cherty magnetic iron formation, which accounts for the major portion of the economic tonnage. However, a reconnaissance gravity survey of the prospect was undertaken to aid in a structural analysis of the property. The gravity survey not only provided information about the regional setting of the iron formation, but also provided useful information about the local structure especially in regards to the non-magnetic hematite and siderite types of iron formation encountered in the drilling. In particular, the gravity investigation was largely responsible for delineating the footwall contact of the iron formation, which without the use of gravity could not have been defined except by expensive drilling through uneconomic, non-magnetic horizons. The limits of the iron-rich formation derived from the gravity survey also suggests that the major areal distribution of the magnetic anomalies is not controlled by structure, but is rather simply due to the distribution of the magnetite-rich horizons within the iron formation.

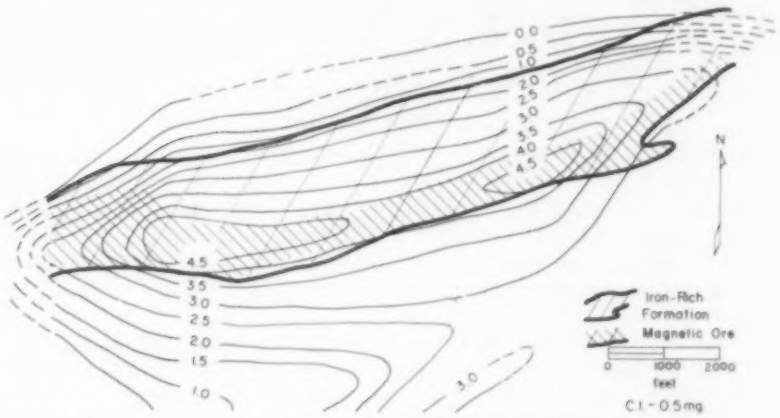

Fig. 9. Residual Bouguer gravity anomaly ($\sigma = 1.8$) map of the Magnetic Center prospect, Marenisco Range, Wis.

Figure 9 is a residual Bouguer gravity map of the prospect with the general outline of the main iron formation as interpreted from the geophysical studies. Core drilling has largely corroborated the interpretation. The outline of the magnetic ore, which is also indicated in the figure, roughly correlates with the peak of the gravity anomaly, which is overemphasized by the shift of the peak of the anomaly to the south of the center of the iron formation due to the southerly dip of the formation.

Example III.—A gravity anomaly profile that has been observed associated with iron formations in some areas of the Lake Superior region is illustrated in Figure 10 in conjunction with the Bending Lake, Ontario, iron formation. This iron formation occurs in a series of schists about 100 miles east of Rainy Lake, Ontario. The iron formation consists primarily of alter-

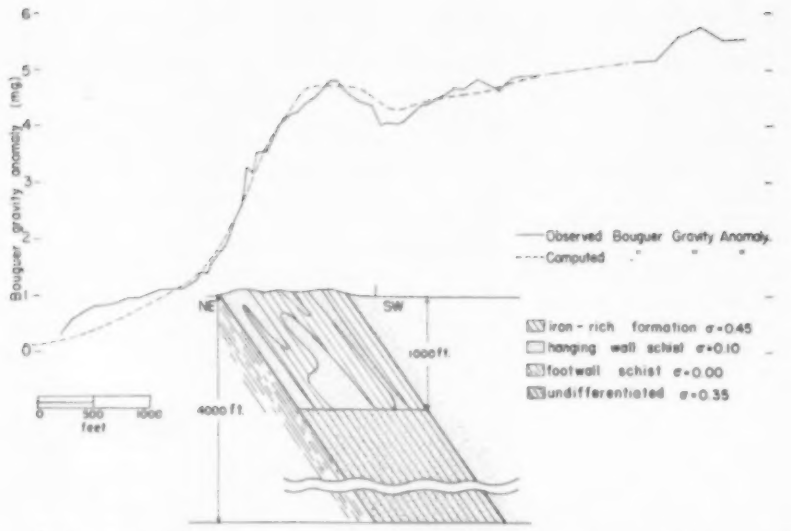

Fig. 10 Observed and computed Bouguer gravity anomaly of the Bending Lake, Ontario prospect

nating bands of quartz and magnetite. Several varieties of schist are associated with the iron-rich rocks, but outcrops and core drilling suggest that the principal types are a garnet schist and a quartz-biotite schist. Outcrops, drilling, and topography indicate that the glacial overburden is thin, rarely exceeding 15 feet.

Two alternative interpretations of the major structure of the iron formation were formulated from a study of the outcrops, core drilling, and magnetic anomalies. The first theory suggests that the iron formation is limited to a rather shallow depth, whereas the second suggests that it extends to a considerable depth. Naturally, these two divergent interpretations lead to different estimates of the tonnage of ore available even through open pit mining operations.

A brief gravity survey was made of a portion of the property in an attempt to resolve the problem of the depth extent of the iron formation. In Figure 10 a composite Bouguer gravity profile over the iron formation corrected for terrain and overburden is shown with a correlative theoretical profile calculated on the basis of the assumed geological section shown in the figure. The components of the iron formation were broken down in detail to a depth of 1,000 feet on the basis of outcrops, drilling, and magnetic data; however, the iron formation was lumped together with the included schist from depths of 1,000 to 4,000 feet which satisfied the purposes of the survey. The close correlation between the observed and calculated anomaly profiles strongly suggests that the iron formation extends to a considerable depth, thus sup-

porting the second geological interpretation, and at least postpones additional core drilling to a more convenient time.

Example IV.—This example was chosen to illustrate the manner in which the gravity method can be used as a reconnaissance tool in the search for regional structures that are favorable for the occurrence of iron ore. The Baraboo syncline, which is an inlier of folded Precambrian igneous and metasedimentary rocks in the flat-lying Paleozoic sedimentary rocks of south-central Wisconsin, contains a relatively non-magnetic iron formation that has been a source of direct shipping iron ore in the past. Similar synclines containing potential iron ores may lie hidden under a veneer of horizontal Paleozoic sediments in this same area.

One method of locating the syncline is illustrated in Figure 11 which is the residual Bouguer gravity anomaly map of the Baraboo syncline region. A distinct gravity minimum reaching a maximum amplitude of − 18 milligals is shown correlating with the syncline. The origin and implications of this minimum are explained elsewhere (8). It is suggested that synclines similar to the Baraboo syncline in the same general area may be isolated by searching for similar negative gravity anomalies.

SUMMARY

The preceding discussion has pointed out the advantages and application of the gravity method to iron ore exploration when the method is used properly and the results are interpreted in light of the methods limitations and

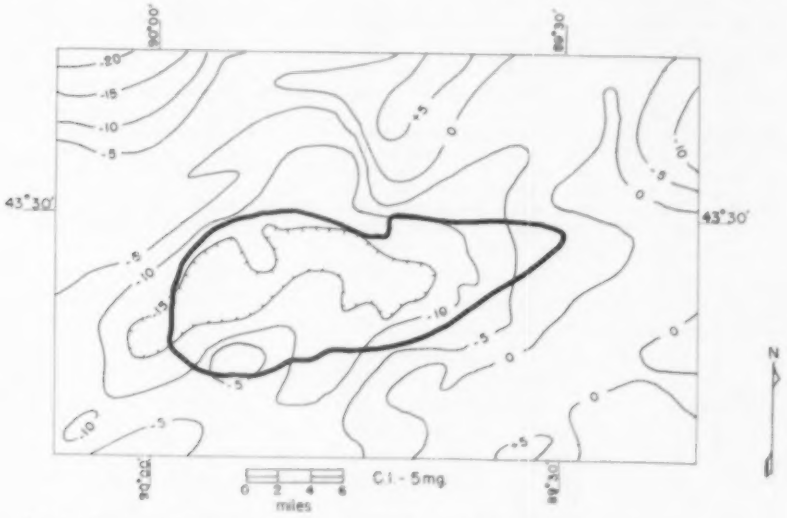

Fig 11 Residual Bouguer gravity map (σ = 2.67) of the Baraboo syncline

the local geological setting. The gravity method has not, however, realized its full potential as a tool in iron ore exploration and probably will not until sufficient data have been gathered and published on surveys covering a wide range of geological conditions and on laboratory and en situ measurements of the density of ores and their country rocks. The full exploitation of such techniques as underground gravity studies and combined gravity and magnetic analysis will also aid the gravity method to reach its full potential.

ACKNOWLEDGMENTS

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MICHIGAN STATE UNIVERSITY,
EAST LANSING, MICH.,
July 14, 1959

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INCLUSIONS IN CASSITERITE AND ASSOCIATED MINERALS[1]

W. M. LITTLE

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ABSTRACT

A study was made of the inclusions in 133 specimens of cassiterite and associated minerals from world wide tin deposits. From the distribution of inclusion types, it would appear that most pegmatitic tin deposits have been formed from siliceous melts, but that most other types of deposits have been formed from aqueous solutions. Since these aqueous solutions had the properties of liquids rather than gases, the deposits are more properly classified as "hydrothermal" than "pneumatolytic." Filling temperature measurements on fluid inclusions indicate that most hydrothermal tin deposition occurs in the 300–500° C range. Of the previously suggested methods of tin transportation, alkali-stannate and alkali thiostannate solutions are in accordance with the inclusion data. Additional possibilities are alkali chloro- and alkali fluo-stannate solutions.

INTRODUCTION

Tin ore deposits are particularly suitable for an investigation of the inclusions in minerals. The main ore mineral, cassiterite, and most of its associated minerals are sufficiently transparent, and coarse grained, for inclusions to be readily observed under the microscope, which is not the case with most other types of ore deposits. Also some of the problems of tin ore genesis have implications of a more general nature. The relations between pegmatites and quartz veins can be studied, since tin deposits occur in both settings, and the question of whether "pneumatolysis" is a major ore forming process can be evaluated, since certain tin deposits are considered by some to be the typical examples for this type of ore deposition.

[1] Extracted from a thesis submitted in conformity with the requirements for the degree of Ph.D. at the University of Toronto, Toronto, Ont.

With few exceptions, tin deposits fall into five fairly well defined morphological (and undoubtably to at least some extent, genetic) classes.

1. Pegmatites. In these deposits the cassiterite is generally closely associated with "replacement" albite, beryl, spodumene, and tantalite-columbite —minerals that are absent in other types of deposits.

2. Normal Tin Veins. This class covers most primary tin deposits, in which the mineralization occurs in quartz veins or their associated alteration zones. The mineralogically similar "pipe" deposits in non calcareous rocks are also included. Characteristic features of these deposits are their close proximity to granitic intrusives, and the common association of wolframite and fluorine-bearing minerals (particularly topaz and fluorite).

3. Deposits in Limestone. These deposits are also closely associated with granites, but "skarn" type silicates are more abundant than quartz, and scheelite and fluorite are much more common than wolframite and topaz.

4. Bolivian Volcanic Type. These deposits are similar to the Normal Tin Veins, except for the absence of nearby granites, the general scarcity of fluorine-bearing minerals, and the relative abundance of sulfides and tin- and silver-bearing sulfo-salts.

5. Mexican Volcanic Type. These deposits are characterized by their occurrence in Tertiary rhyolite flows, and by the presence of minerals typical of fumaroles, such as specularite, cristobalite and tridimite.

This classification was used as a framework for the inclusion study, with a twofold purpose in mind. The inclusion work could be expected to provide some information on the extent of the genetic differences between the classes. Also some of the geological features shown by the different classes, particularly those pertaining to probable depths of formation, have an important bearing on the interpretation of some of the inclusion data.

The inclusion study involved the examination of 133 specimens, from 80 different localities, which include all major past or present producing districts outside of Russia and China. The work, however, was of a reconnaissance nature. Only a few speciments were examined from any single deposit, and only the more readily determined features of the inclusions were investigated. Considerably more work on the details of individual deposits, and the chemical composition of inclusions could be done, and would seem well worth-while.

ACKNOWLEDGMENTS

The experimental work was carried out under the direction of Dr. F. G. Smith, who gave numerous suggestions. Funds were supplied for the construction of the heating stage by the National Advisory Committee on Research in the Geological Sciences, and for the purchase of specimens by the Department of Geological Sciences, University of Toronto.

The following individuals and mining companies were most obliging in donating specimens: Mr. F. Ebbutt; Professor G. M. Brownell; Dr. Y. B. Fortier; Dr. H. S. Bostock; Mr. C. L. Sainsbury; Mr. J. McAndrews; Patino Mines and Enterprizes Ltd.; Mr. G. Collins; Dr. H. Frohberg; Mr. N.

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PREVIOUS WORK

Literature on inclusions in cassiterite is virtually non existent. The following sentence is the only reference found on the microscopic observation of fluid inclusions—"Tin ore contains many excellent fluid-cavities, though they are usually very small" (*37*, p. 474). Decrepitation tests were carried out by Smith (*28*) on one specimen of cassiterite from Cornwall, and a sharp "break" in the rate curve at 345° C was considered to be caused by the filling of fluid inclusions.

There is additional information on the inclusions in other minerals from tin deposits. Hunt (*13*) described inclusions that contain a liquid, a bubble, and in some cases a salt crystal, in quartz veins from Cornwall. Grootoff (*7*, pp. 9–11) observed two-phase fluid inclusions in quartz associated with the deposits of Billiton, Indonesia, and found that the gas given off on heating specimens to 750° C was steam with a little CO_2, and minor amounts of Cl_2 and H_2S. Smith (*28*) tested quartz, tourmaline, wolframite and chalcopyrite from Cornwall by the decrepitation method, and obtained readings varying from 261 to 345° C. The decrepetation was thought to be caused by the filling of fluid inclusions, since in a thin section of the quartz, two phase fluid inclusions were observed, and the filling temperatures estimated from the bubble-liquid ratio was close to the decrepitation temperature. Konta (*19*), using the decrepitation method, obtained readings of 294–304° C on four specimens of quartz, and 277° C on two specimens of fluorite from a tin deposit in Zinnwald. Two phase fluid inclusions were observed in thin sections of these minerals, and the decrepitation results were interpreted as representing filling temperatures.

METHODS OF EXAMINATION

Thin sections of all suitable specimens were examined under the microscope using a magnification of 1,000 ×. The thin sections were polished on both sides, and vary in thickness from .3 to 3 mm, depending on the transparency of the mineral. With this type of section, good to excellent resolution of inclusions was obtained in most cases—the exceptions being the wolframite specimens and some of the pegmatitic cassiterite.

Most inclusions were examined over the temperature range of about 10 to 40° C, to check for any changes in the number or relative amount of the fluid phases. The heating and cooling was done on the microscope stage, temperatures above room temperature being obtained by pressing a hot spatula against the top of the section, and the lower temperatures by use of an ethyl chloride spray. A few inclusions were examined at considerably lower temperatures by cooling the section by means of liquid air, and observing it under the microscope as it returned to room temperature.

In a few cases measurements were made on the temperatures of phase changes that occur below room temperature by means of a cooling stage. The specimen and a concentrated $CaCl_2$ solution, which had been cooled by dry ice, were placed in a glass dish on the microscope stage, and the temperature was measured as it rose to room temperature by a thermometer, which also served as a stirring rod.

The filling temperatures of fluid inclusions were determined in four ways:

Heating Stage Measurements.—The air-heated heating stage that was constructed for the study, is shown in Figure 1. It was calibrated with a Thomas "Micromelt" set, and by observing the melting temperatures of thin shavings of tin, lead, and zinc. With these calibrating materials results were reproducible to ± 3° C, but a somewhat lower accuracy could be ex-

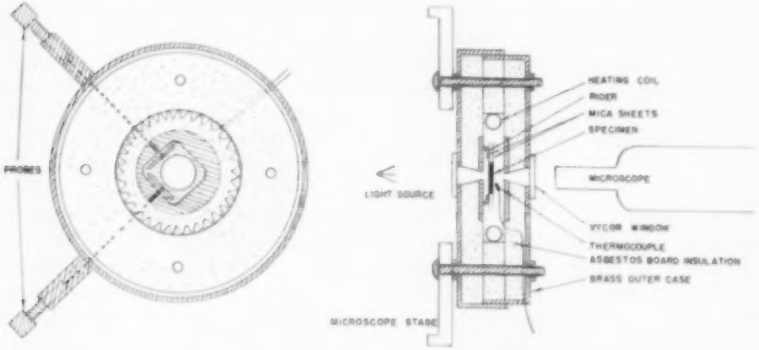

FIG. 1

HEATING STAGE

pected with thin sections of minerals because of their variation in size. The stage was attached to a microscope with a Leitz UM 4 long focus objective and 15 power occular, giving a magnification of 450 ×.

Using the heating stage, filling temperature measurements were made on all fluid inclusions of sufficient size for accurate observation. To check against the possibility of partial leakage occurring during the heating stage test, duplicate measurements were made in all cases, and a comparison was made of the size of the bubbles in the inclusions before and after heating.

The heating stage method of determining filling temperatures has several practical disadvantages. It is only applicable to transparent minerals, it is time consuming, the 450 × magnification used only allowed about 1 percent of the observed inclusions to be tested, and inclusions sometimes leak during heating. It has the outstanding advantage, however, of being the only method that gives a direct measurement of the filling temperature, and all other methods proved to be either unreliable or impractical.

Calculations from Bubble-Cavity Ratio.—In this method, which was applied to all fluid inclusions of suitable size and shape, the dimensions of the bubble and cavity are measured using a micrometer occular, their relative volumes are calculated, and the filling temperature is obtained using P-V-T data for water.

Although this method has the advantages of being more rapid than the heating stage tests, and can be applied to smaller inclusions, it has very severe limitations. Volume calculations are only possible with inclusions of regular shape, and large errors are involved because of the differences between the P-V-T relations of pure water and the solutions actually present in the inclusions. In practice, it was found that this method almost always gave lower filling temperatures than the heating stage method (the error usually being 50° and at times over 100° C), which is almost certainly a result of the inclusions containing water solutions of non-volatile compounds, rather than pure water.

Although the quantitative results obtained by this method are unreliable, they are of some value, since they allow inclusions too small for the heating stage method to be related to those on which heating stage tests were made.

Estimates from Bubble-Cavity Ratio.—In this method, a visual estimate is made of the filling temperature from the apparent bubble-cavity ratio (to which the filling temperature is related). In the early stages of the study, this was done by comparing actual inclusions with a diagram showing hypothetical inclusions of various shapes, bubble-cavity ratios, and calculated filling temperatures, but with practice it was found that the diagram could be dispensed with. The estimates were made before other methods were applied, to minimize subjective errors.

This method is very rapid, and can be applied to any fluid inclusion of sufficient size for the bubble to be observed. The results are quite close to that of the calculation method, the difference in most cases being less than 30° C. However being based on P-V-T data for pure water it is subject to the same errors as the calculating method, and the estimated filling temperatures are of value only in that they allow small inclusions to be compared with the larger ones on which the heating stage tests were made.

Decrepitation Method.—This method of determining the filling temperature of fluid inclusions is described by Scott (22), Peach (20) and Smith and Peach (36). It has the practical advantages of being rapid, the results give an average value of a large number of inclusions, inclusions too small for heating stage determinations can be tested, and it can be applied to opaque as well as transparent minerals. It has the disadvantage, however, that in some cases, decrepitation caused by the filling of primary inclusions can be masked by that of secondary inclusions, or by the "anonalous" decrepitation described by Smith and Little (34).

In the present study, the "anonalous" decrepitation severely limited the usefulness of the method. Decrepitation of this type, which is a feature of almost all hydrothermal minerals, starts in the 250–300° C range and reaches a peak at about 375° C, irrespective of the filling temperatures of observable

fluid inclusions. Since the filling temperatures of the primary inclusions in cassiterite and associated minerals (as determined by the heating stage measurements) are also usually in the 250–400° C range, the decrepitation results generally could not be interpreted.

RESULTS

The types of inclusions in the specimen, and the filling temperature results are listed in Tables I–IV. For both the measured (heating stage determinations) and calculated filling temperatures, the limits of variations refer to the differences between the different inclusions in the specimen, rather than the probable errors involved. Because of the problems in interpretation, the decrepitation results are not recorded.

Several different types of inclusions were observed.

H_2O Inclusions.—The most common type of inclusion found, is the normal two-fluid phase type, which at room temperature contains a liquid and a bubble. In all cases, the size of the bubble was less than 40 percent of the volume of the cavity. No additional fluid phases developed on cooling the specimens with the ethyl chloride spray, or in the 7 specimens that were cooled to much

TABLE I

SPECIMENS FROM PEGMATITES

Specimen			Types of Inclusions	Filling Temperatures			
				Estimated	Calculated		Measured
No.	Mineral	Locality		T°C.	Vol. Anal. Vol. Liq.	T°C.	T°C.
4	Cassiterite	Rose L., N. W. T., Can.	"Complex", Some rutile				
8	"	Keystone, S. D., U.S.A.	"Complex"				
9	"	" " "	"Complex"				
	Quartz		H_2O S(?), some "complex"				
	Albite		"Complex", some H_2O?				
11	Cassiterite	Minas Geraes, Brazil	H_2O S(?)	180-200			
			H_2O P(?)	300	1.33	280	
			Rutile				
12	Cassiterite	Uis Mine, S. W. Africa	"Complex", some rutile				
	Quartz		H_2O S(?)	175			
			"Complex"				
			H_2O-CO_2 II				
13	Cassiterite	Ameib Mine, Erongo, S. W. Africa	"Complex"(?)				
			H_2O P(?)	300			
	Quartz		H_2O P(?)	300			
			H_2O-CO_2(?)				
14	Cassiterite	Hundingamo, S.W.Africa	"Complex"(?)				
	Quartz		H_2O S(?)				
15	Cassiterite	Omhako, S. W. Africa	H_2O P(?)	300	1.62	325	
			Rutile				
	Quartz		H_2O S(?)	175-250			
			Tourmaline				
16	Cassiterite	Manomo, Matanga	H_2O P(?)	270	1.22	230	
			"Complex"				
17	Spodumene	" "	H_2O P	230	1.74	345	346
18	Quartz	" "	H_2O S	100			
			H_2O P(?)	300			
19	Quartz	" "	H_2O S(?)	180			
20	Amblygonite	Barenga, Ruanda	H_2O P(?)	300			313
21	Quartz	" "	H_2O S	100			
			H_2O P(?)	300			
22	Beryl	Chanderiang area, Perak, Malaya	H_2O S(?) very few,	110			
			H_2O-CO_2 II) - abundant,(a few		1.89		346
			H_2O-CO_2 I and II)				
23	Cassiterite	" "	H_2O P(?) some with large salt crystals and smaller anisotropic crystals.	300	1.30	270	361
			H_2O-CO_2 I P(?)		2.22 -4.83		366

Note: Seven additional cassiterite specimens examined but found to be too opaque to observe any inclusions present.

TABLE II

SPECIMENS FROM NORMAL TIN VEINS

Specimen No.	Mineral	Locality	Types of Inclusions	Filling Temperatures Estimated T°C.	Calculated Vol. Incl. Vol. Liq.	T°h	Measured T°C.
24	Cassiterite	Uncia, Bolivia	H_2O F, some with salt xls.	340	1.41	332	346
25	"	Rosario Vein, Asiento, Bolivia	H_2O F, very few H_2O+CO_2(?)	340	1.54	330	342
	Quartz		H_2O F, very few H_2O+CO_2(?)	320			328
26	" (smoky)	S. Terrace Vine, Cornwall	"Complex"				
27	Cassiterite	L. Crofty Vine, Cornwall	H_2O F(?)	290	1.22	230	
	Quartz		H_2O F(?)	280	1.45	310	
28	"Capped" quartz from granite.	St. Austell, Cornwall	H_2O S(?) "Complex"				
29	Quartz (Amythest)	S. Terrace Vine, Cornwall	H_2O S(?) few H_2O F(?) few "Complex" - numerous	330			
30	Cassiterite	L. Crofty Vine, Cornwall	H_2O F(?)	250	1.39	260	
31	Quartz, from cross course	S. W. Cornwall	H_2O S(?) H_2O F(?) "Complex"	130 200			
32	Zinnite	St. Austell, Cornwall	H_2O F	280	1.43	300	
33	Quartz	Castle-an Dinas Vine, Cornwall	H_2O F(?), some with salt xls., and anisotropic xls. H_2O+CO_2(?)	240			
34	Sphalerite	Cornwall	H_2O F(?)	100			
	Quartz		H_2O F(?), a few with anisotropic crystals	140			
35	Fluorite	Cornwall	H_2O S(?)	130			
36	Quartz	Cornwall	H_2O F(?), some with salt xls.	300			
37	Quartz	Cornwall	H_2O S(?) few H_2O F - some with salt and anisotropic xls. H_2O+CO_2F	300			
38	Quartz	Cornwall	H_2O S(?) H_2O F(?) some with salt and anisotropic xls.	300			
	Fluorite		H_2O S(?)	150			251
			H_2O F(?) some with salt and anisotropic xls.	270	1.40	300	298
39	Quartz, from granite	Cornwall	H_2O S(?)	130-300			
40	Cassiterite	Cornwall	H_2O F(?)	300	1.35	290	304
							409
42	Sphalerite	Cornwall	H_2O F(?)	180	1.11	170	
43	Wolframite	Cornwall	H_2O S(?)				
			H_2O F(?)	280	1.24	225	
44	Cassiterite	"	H_2O F(?) some with salt xls. H_2O+CO_2(?) a few	290	1.33	250	308
	Quartz		H_2O S(?)		2.54		
			H_2O F(?) H_2O+CO_2(?) Tourmaline	275	1.33	260	409
45	Cassiterite	"					
46	"	Ehrenfriersberg, Erzgebirge	H_2O F(?)	270	1.30	260	
47	Apatite	"	H_2O S(?)	160	1.06	110	169
			H_2O F(?)	320			357
							424
							399
48	Cassiterite	Preuden, Erzgebirge	H_2O+CO_2(II) F(?) H_2O+CO_2 II F		1.09		364
	Quartz		H_2O S(?)	160			
			H_2O F(?)	320	1.16	300	
49	Cassiterite	Freiberg, Erzgebirge	H_2O F(?)	340	1.47	340	406
50	Topaz	Schneckenstein, Erzgebirge	H_2O F(?)	320	1.62	345	395
			H_2O+CO_2 (?) F(?)		3.10		
51	Topaz	Altenberg, Erzgebirge	H_2O F(?) some with salt xls.	330	1.64	334	
	Quartz		H_2O S(?) some with anisotropic xls.	200			
52	Quartz, from veinlet	Zinnwald, "	H_2O F(?) some with salt xls. H_2O+CO_2(?) F(?)	350	1.77 2.80	350	
53	Quartz	" "	H_2O F(?)	200-300			325
			H_2O+CO_2 (?) F(?) few				
54	Cassiterite	Lombrales, Spain	H_2O F(?)	260-310	1.52	328	315
55	Cassiterite	Jabrosa, Portugal	H_2O F(?)	275	1.27	260	280
	Quartz		H_2O S(?)	180			
			H_2O F(?)	250	1.21	230	
56	Cassiterite	Pregaens, Portugal	H_2O F(?)	240	1.19	215	
	Quartz		H_2O S(?)	170	1.10	160	
			H_2O F(?)	250	1.23	230	
57	Cassiterite	Durchen, France	H_2O F(?)	360	1.37	360	
58	"	Bauchi, Nigeria	H_2O F(?), some with salt xls.	260	1.24	240	
59	"	Camp Akenis, Belgian Congo	H_2O F(?)	350	1.30	320	
60	Wolframite	" " " "	H_2O F(?)	180			

TABLE II (continued)

61	Topaz	Camp Atende, Belgian Congo	H_2O P(?)					518
			H_2O-CO_2 I P(?) rare		6.06			569
62	Quartz	" " " "	H_2O S	190				
			H_2O P(?) some with salt xls.	280				347
			H_2O-CO_2 I P(?)					196
63	Cassiterite	Camp Miesho, " "	H_2O S(?)		1.31	280		334
			H_2O P(?)					270
64	Cassiterite	" " " "	H_2O P(?)	230				266
65	"	" " " "	H_2O P(?)	260	1.23	240		344
66	Quartz	" " " "	H_2O S(?)					206
			H_2O P(?)	295	1.13	190		365
			H_2O P(?)					
			H_2O-CO_2 II P(?)					
67	Cassiterite	Camp Mankuku, " "	H_2O S(?)		1.10	180		305
			H_2O P(?)		1.45	310		366
			H_2O-CO_2 I P(?)		2.75			175
68	"	" " " "	H_2O P(?)		1.20	230		237
			H_2O P(?) with salt crystals					494
			H_2O-CO_2 I and II P(?)		4.60			346
69	"	Camp Tshali, " "	H_2O S (?)	190				
			H_2O P(?) some with salt xls.	300	1.43	310		
70	"	" " " "	H_2O S(?)		1.18	210		
			H_2O P(?)		1.33	280		421
71	"	Camp Manisuku, " "	H_2O P(?)					
72	"	" " " "	H_2O P(?)	200				
73	"	Camp Kabitaka, " "	H_2O P(?)	200				
74	"	" " " "	H_2O P(?)	300				
			H_2O P(?)					361
75	Topaz	" " " "	H_2O P(?)	250	1.21	230		
76	Wolframite	Camp Kanyama, " "	H_2O P		1.26	256		
77	Cassiterite	Camp Musala	H_2O P(?)		1.35	256		259
78	Cassiterite	Tuberaka, " "	H_2O P(?), some with salts xls.					353
79	"	Camp Atende, " "	H_2O P(?)	280				160
80	"	" " " "	H_2O P(?)	290				
81	"	" " " "	H_2O P(?)		1.35	290		
82	"	Avanga, " "	H_2O P(?)		1.28	256		
83	"	Camp Mankuku, " "	H_2O P(?)		1.66	316		353
			H_2O P(?) with salts xls.		1.22	250		
			H_2O-CO_2 I P(?) common		5.35			347
84	"	Camp Miesho, " "	H_2O P(?)	175				
85	"	" " " "	H_2O P(?)	175	1.23	240		367
86	"	Camp Kasiroku, " "	H_2O P(?)	200	1.49	320		362
87	"	Avanga, " "	H_2O P(?)		1.26	256		
88	Quartz	Kallo, Kanioma, " "	H_2O P(?)	250	1.33	260		510
89	"	Kroube, Kanioma, " "	H_2O P with salt xls, some with anisotropic xls.	230				
90	Cassiterite	" " " "	H_2O P(?) some with salt xls.	220				362
91	Cassiterite	Klute, Malaya	H_2O S(?)	190	1.11	170		
			H_2O P(?) some with salt xls.	260	1.24	250		
			H_2O-CO_2(?) P(?)		2.33			
	Quartz		H_2O S(?)	150				
			H_2O P(?) some with salt xls.	260				
			H_2O-CO_2(?) P(?)					
92	Cassiterite	Mangkobu, Malaya	H_2O S(?)	150				
			H_2O P(?) some with salt xls.	280	1.19	230		
			H_2O-CO_2(?) P(?) few					
93	Cassiterite	Selangor, Malaya	H_2O P(?) few					
	Quartz		H_2O S(?)	100				
			H_2O P(?) some with salt xls.	220	1.11	170		
			H_2O-CO_2(?) P(?)					
94	Cassiterite	Gunung Bapat, Perak, Malaya	H_2O S(?)		1.11	170		
			H_2O P(?)	260				
95	"	Klappa-Empit Mine Billiton, Indonesia 1st. level. E. Sect.	H_2O P(?)	240				
			H_2O-CO_2(?) P(?) few					
	Quartz		H_2O P(?)	260	1.17	210		
96	Cassiterite	4th level, E. Section	H_2O P(?)	260	1.33	260		
97	"	4th level, E. Section	H_2O S(?) few	160				
			H_2O P(?)	240	1.17	210		
98	"	5th level, E. Section	H_2O P(?)	220	1.17	210		188
	Quartz		H_2O P(?) some with salt xls.	240	1.15	195		
99	"	9th level, E. Section	H_2O P	190	1.14	190		228
100	Fluorite	9th level	H_2O P(?)	100				60
101	Cassiterite	Tikus, E. Billiton, Indonesia	H_2O P(?) some with salt xls.	270	1.26	251		
	Quartz		H_2O P(?) some with salt xls.		1.19	217		
102	Cassiterite	Aruemsang Mine, E. Billiton, Indonesia	H_2O P(?) some with salt xls.	210	1.14	190		
103	"	Tenterfield, N. S. W., Australia	H_2O P(?)	275	1.30	270		
104	"	Emmaville, N. S. W., Australia	H_2O P(?) some with salt xls.	250	1.15	195		
	Quartz		H_2O P(?)	270				
105	Cassiterite	Lyell, N. I. C., Australia	H_2O P(?)	280				
	Quartz		H_2O P(?) some with salt xls.	200-300				286
								408
106	Cassiterite	Mt Bischoff, Tas., Australia	H_2O S(?)					
			H_2O P(?) some with salt xls. tourmaline	230				
	Tourmaline		H_2O P(?)	300				
107	Quartz	W. Coast, Tas., Australia	H_2O S(?) common, some with salt xls.	135	1.06	170		
			H_2O P(?) few	320				
108	Tourmaline	W. Coast Tas. Australia	H_2O S	190				
			H_2O P(?)	300				
109	Cassiterite	Aberfoyle Mine, Tas., Australia	H_2O P(?)	230				288
			H_2O-CO_2(?) few					
110	Scheelite	" " "	H_2O P(?)	190				148
111	Fluorite	" " "	H_2O P(?)	100				160
112	Wolframite	" " "	H_2O P(?)		1.36	290		
	Quartz		H_2O P(?)		1.19	280		291
113	Cassiterite	Storrie Ck., Tas., Australia	H_2O P(?)		1.48	310		288
			H_2O-CO_2 P(?)		2.48			334

Note: One additional cassiterite specimen examined but found to be too fine grained for any inclusions present to be observed.

TABLE III

SPECIMENS FROM DEPOSITS IN LIMESTONE

Specimen			Types of Inclusions	Filling Temperatures			
				Estimated	Calculated		Measured
No.	Mineral	Locality		T°C.	Vol. Incl. Sol. Liq.	T°C.	T°C.
114	Cassiterite	Gorman Dist., Cal., U. S. A.	H_2O P(?) some with salts xls.		1.28	250	
115	"	Lost River, Alaska	H_2O-CO_2(?) P(?) few H_2O P(?)		1.37	280	339
	Fluorite		H_2O S(?)	150			
116	Cassiterite	" " "	H_2O P(?)	300	1.28	260	
	Fluorite		H_2O P(?)	275	1.31	270	
			H_2O S(?)	100			
			H_2O P(?)	300			
117	Cassiterite	Campiglia, Italy	H_2O P(?)	230	1.22	230	
118	"	Arandis, S. W. Africa	H_2O P(?) H_2O-CO_2(?) P(?)	230	1.18	210	
119	"	Perak, Malaya					
120	"	Ipoh Dist., Perak, Malaya	H_2O P(?) most with salt xls. H_2O-CO_2(?) P(?) only one	220	1.19	215	

TABLE IV

SPECIMENS FROM BOLIVIAN VOLCANIC DEPOSITS

Specimen			Types of Inclusions	Filling Temperatures			
				Estimated	Calculated		Measured
No.	Mineral	Locality		T°C.	Vol. Incl. Sol. Liq.	T°C.	T°C.
121	Cassiterite	Contacto Vein, Llallagua, Bolivia 555 m. level	H_2O P	300			
122	"	446 "		300	1.45	310	
123	Quartz	" "	H_2O S	140			110
			H_2O P	350			379
124	Quartz	481 "	H_2O S	140			140
			H_2O P	350			345
125	Quartz	551 "	H_2O S(?)	140			
			H_2O P	300	1.41	300	
126	Cassiterite	Llallagua, Bolivia	H_2O P(?) with salt xls.	200-300	1.18	210	
					1.41	300	400
127	Wolframite	" "	H_2O P(?)	230	1.17	210	
128	Apatite	" "	H_2O S(?)	140	1.10	145	
			H_2O P(?)	280	1.28	260	298
129	Cassiterite	Cajila Mine, Bolivia	H_2O S(?)	150 25			
			H_2O P(?)	275	1.25	240	
131	Quartz	Potosi, Bolivia	H_2O S(?)	150			
			H_2O P(?)	300	1.13	180	

Note: Three additional cassiterite specimens examined but found to be too fine grained for any inclusions present to be observed.

lower temperatures (well below the freezing point of the liquid) by means of liquid air. On heating inclusions of this type, the bubble contracts until it disappears. Cubic, isotropic crystals may be present in the liquid, and in some cases are accompanied by smaller anisotiopic crystals. Examples of these inclusions are shown in Figures 2–9.

The identification of the liquid in inclusions of this type as a water solution, has been almost universally accepted in the literature, and is on firm grounds. In a few cases positive identification has been made by chemical analysis (3, 26, 18, 8). The phase changes that accompany changes in temperature (freezing point and filling temperature measurements) are in all cases in accordance with P-V-T data for water solutions, and demonstrate that the liquid is not any of the other fluids of conceivable geological importance (CO_2, CO, H_2S, SO_2, SO_3, HCl).

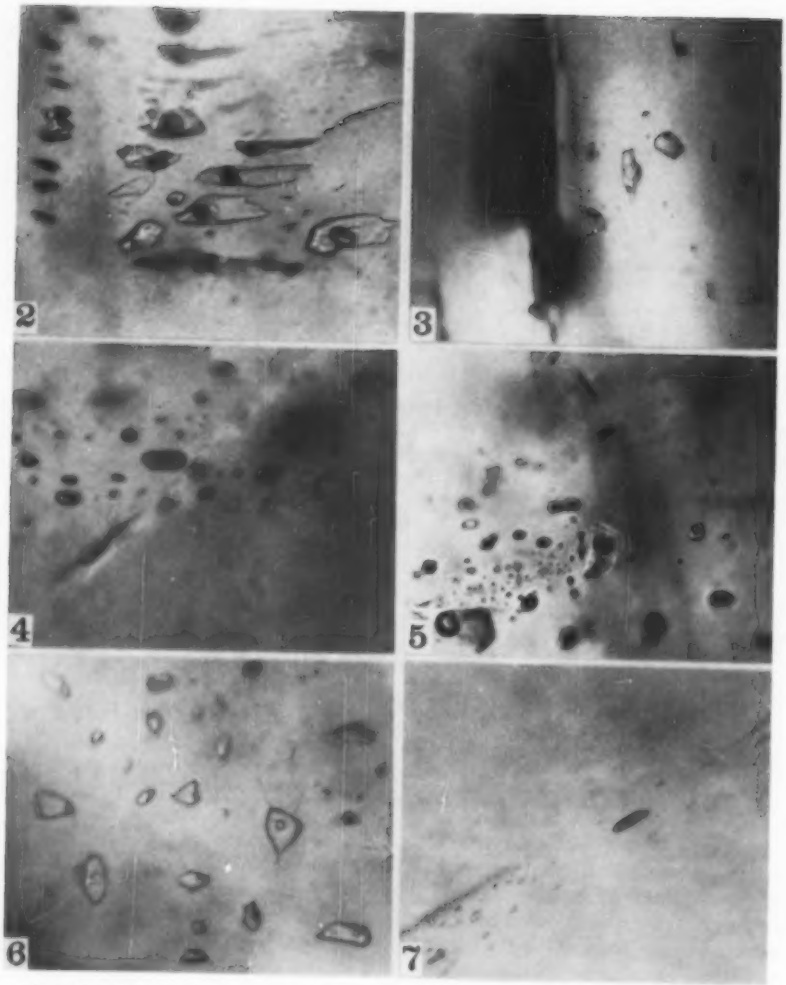

FIG. 2. H_2O inclusions, apatite spec. 129, Llallagua, Bolivia, filling temperature $352 \pm 2°$ C, $\times 750$.

FIG. 3. H_2O inclusions, cassiterite spec. 127, Llallagua, Bolivia, filling temperature $400 \pm 6°$ C, $\times 750$.

FIG. 4. H_2O inclusions, cassiterite spec. 40, Cornwall, filling temperature $499 \pm 15°$ C, $\times 750$.

FIG. 5. H_2O inclusions, fluorite spec. 38, Cornwall, filling temperature $398 \pm 7°$ C, $\times 750$.

FIG. 6. H_2O inclusion, scheelite spec. 110, Aberfoyle Mine, Tasmania, filling temperature $148 \pm 4°$ C (note small bubbles), $\times 500$.

FIG. 7. H_2O inclusions, cassiterite spec. 86, Belgian Congo, filling temperature $352 \pm 3°$ C, $\times 750$.

The determination of the composition of the bubble in these inclusions is a more difficult problem. While it is probably essentially water vapour in most cases, other gases could be present, and as will be discussed below, there is indirect evidence for this in some specimens.

H_2O-CO_2 Inclusions.—In some specimens, inclusions were found in which a third fluid phase appears at some temperature below 31° C. This has usually been interpreted as indicating the presence of substantial amounts of CO_2 in the inclusion, the three phases being considered to be essentially water, liquid CO_2 and CO_2 gas.

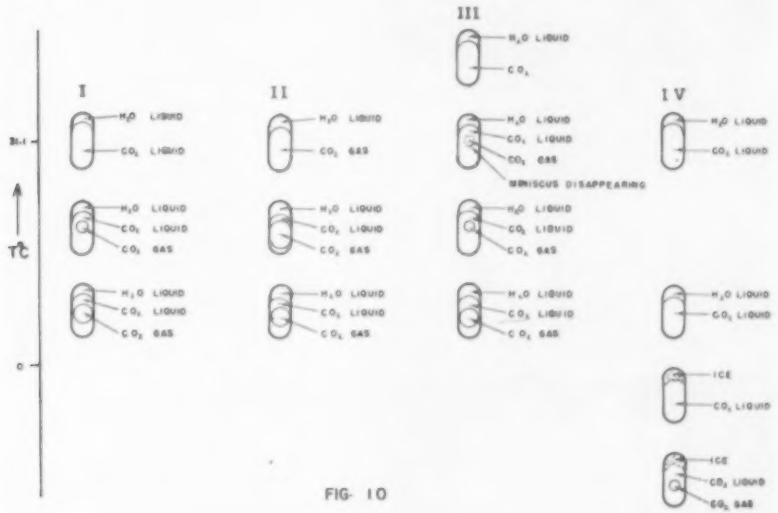

FIG. 10

TYPES OF H_2O-CO_2 INCLUSIONS

As is shown in Figure 10, the transformation from the 3 phase to 2 phase condition can occur in four ways. The CO_2 gas bubble can contract until it disappears (Case I), expand until no liquid CO_2 is left (Case II), or the interface between the CO_2 phases can fade out (Case III). Case IV transformations, which were observed in one specimen, are essentially the same as Case II transformations, the difference being that the CO_2 gas bubble disappears by contraction below rather than above the freezing point of the water solution. This type of transformation has not been previously reported in the literature, but this is probably because it has not been looked for. Case II transformations can probably also occur below the freezing point of the water phase, although no examples have been reported.

At higher temperatures (usually in the 300–400° C range), inclusions of this type show a 2 phase to 1 phase transformation, or "filling." This transformation can also occur in three general ways, either by the contraction of

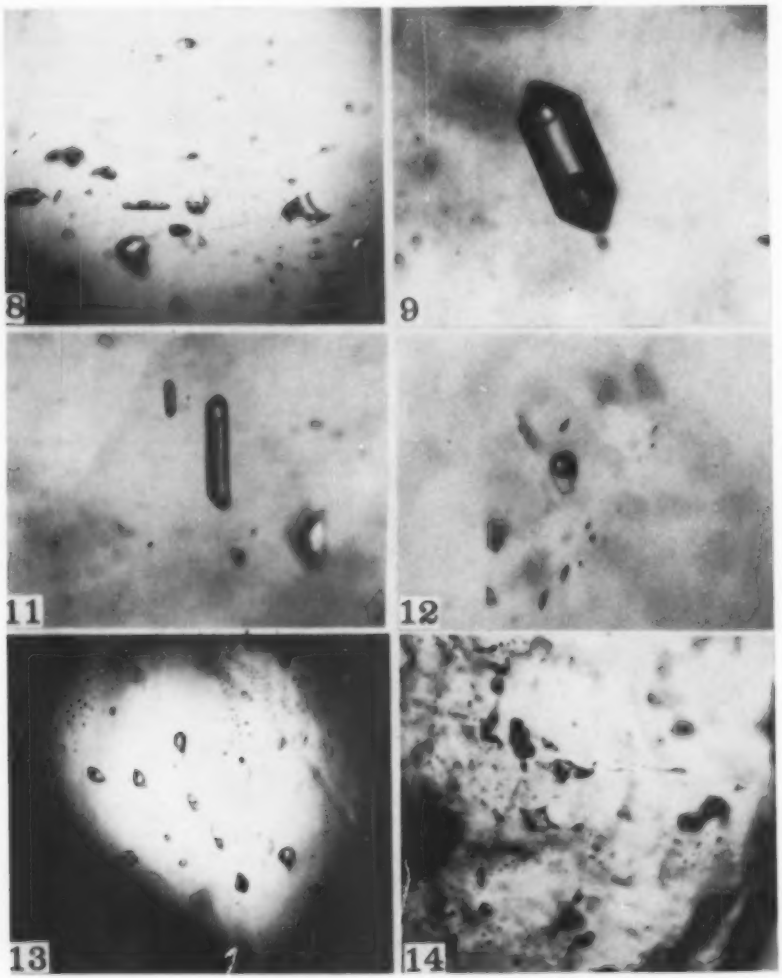

FIG. 8. H_2O inclusions, topaz spec. 61, Belgian Congo, filling temperature $318 \pm 5°$ C, $\times 750$.

FIG. 9. H_2O inclusion, cassiterite spec. 83, Belgian Congo, filling temperature $353 \pm 33°$ C (note salt crystal), $\times 750$.

FIG. 11. H_2O-CO_2 inclusions, cassiterite spec. 83, Belgian Congo. Same specimen as in Figure 9. Filling temperature $347 \pm 3°$ C. (Note large bubble.) $\times 750$.

FIG. 12. H_2O-CO_2 inclusion, beryl spec. 22, Malaya, in three phase condition. Filling temperature $346 \pm 12°$ C, $\times 750$.

FIG. 13. H_2O-CO_2 inclusions, cassiterite spec. 48, Graupen. Filling temperature $364 \pm 3°$ C, $\times 500$.

FIG. 14. Complex inclusions, cassiterite spec. 9, Keystone, S. D., $\times 500$.

the bubble until it disappears, the expansion of the bubble until it fills the cavity, or by the fading out of the interface. The manner in which the filling occurs, is independent of the type of 3 phase to 2 phase transformation which occurred at lower temperatures.

The identification of the phases in these inclusions shown in Figure 10, is on firm grounds. Case III 3 phase to 2 phase transformations are indicative of critical conditions, and in all cases in which measurements have been made on the temperature of such transformations (this was done on inclusions in one specimen, number 22, in the present study, and other examples are reported by Sorby (38), Hartley (9, 10, 11), Erhard and Stelzner (5), and Johnsen (15)), the results have been within 2° C (a reasonable experimental error) of the critical temperature of CO_2. Observations on the temperatures at which other types of 3 phase to 2 phase transformations occur, and on the manner in which the relative amounts of the two interior phases vary with temperature (which were carried out in 9 specimens 22, 23, 47, 48, 61, 67, 68, 83, 129 in the present study and many other examples are listed by Smith (31)), are in accordance with the P-V-T data for CO_2, but not any other geologically probable fluids. The water and liquid CO_2 phases in one inclusion were identified by Brewster (1) by index of refraction measurements. The freezing tests carried out on six specimens (23, 47, 61, 67, 83, 129) in the present study also provide fairly positive identification of the water phase. Although the actual melting temperatures were not measured, they were shown by the cooling stage work to be below 0° C (the lower practical limit of the apparatus due to frost formation), but by the liquid air tests to be well above − 56° C, the melting point of the solid CO_2 in the inclusions. These results are in agreement with the melting temperatures of water solutions, but not of any other geologically probable fluids.

Examples of inclusions of the H_2O-CO_2 type are shown in Figures 11, 12 and 13. They generally have tubular or negative crystal forms, and are similar in size and shape to those of the H_2O type. However, there is a marked difference in the relative size of the bubbles of the two types of inclusions, when they are observed in the 2 phase condition at room temperature (usually slightly over 30° C because of heat derived from the substage lamp of the microscope). All inclusions with bubbles occupying over 60 percent of the cavity on which cooling tests were made, were shown to be of the H_2O-CO_2 type (i.e., a third phase appeared). All tested inclusions with bubbles occupying less than 40 percent of the cavity were shown to be of the H_2O type (i.e., no additional phase appeared). Because of this relationship, inclusions that were too small for the cooling tests, but which had bubbles occupying over 60 percent of their cavities, are considered to be likely of the H_2O-CO_2 type, and are referred to in Table 1–3 as "H_2O-CO_2(?)" inclusions.

Complex Inclusions.—Examples of these inclusions are shown in Figure 14. Their contents consist for the most part of crystalline material (which is mostly anisotropic) but relatively small bubbles (one-quarter of the volume of the cavity or less) are generally also present. The outlines of these inclusions are irregular, and markedly different from the rounded tubular, or negative crystal

forms of H_2O and H_2O-CO_2 inclusions. They will be referred to as complex inclusions.

In a number of specimens of pegmatitic cassiterite, inclusions with ragged outlines were observed, which may be of this type, but because of the dark color of the cassiterite and the small size of the inclusions, it was not possible to determine whether they contained crystals. These are referred to in Tables I–V as complex(?) inclusions.

It has not been possible to identify the contents of these inclusions, but the only likely interpretations are that they represent the entrapment of either a siliceous melt or an extremely highly concentrated water solution. They are similar to the inclusions observed by Smith (29) in garnet, which were considered to indicate deposition from siliceous melts, and other examples have been observed in beryl (Smith, F. G., personal communication).

Solid Inclusions.—Inclusions consisting of solid material only are not common in cassiterite. In a few cases small crystals of tourmaline were observed, and some of the cassiterite from "limestone" deposits contains tremolite. Pegmatitic cassiterite may contain small crystals of a reddish brown mineral, which is tentatively identified as rutile.

Primary and Secondary Inclusions.—The distinction between inclusions were trapped at the time of crystal growth, and those that formed in cracks at some later time, is obviously of fundamental importance in the interpretation of inclusion data. In some cases this distinction can be made with assurance. Inclusions not distributed in planes are probably primary, and those in planes that cross grain boundaries are obviously secondary. However inclusions commonly occur in planes that do not cross grain boundaries, and may be primary(having formed in growth or lineage planes), or secondary (since there is no necessity for a crack to cross a grain boundary).

Although almost all of the fluid inclusions observed in the present study are of the latter indefinite type, there are a number of reasons for believing that most are primary.

1. The inclusions that occur in planes, in almost all cases appear to be identical in size, shape, contents and filling temperature, to the inclusions that are not distributed in planes, and are almost certainly primary.

2. The temperature of deposition range (300–500° C) indicated by the filling temperature measurements if the inclusions are assumed to be primary, is geologically reasonable.

3. Most of the specimens are crystals that grew into open cavities, and although this does not eliminate the possibility of cracks and secondary inclusions, the chances of this occurring are greatly reduced.

4. The general similarity in size, shape, distribution and filling temperatures of all of the fluid inclusions observed in cassiterite and associated minerals, suggests that with a few exceptions, they were all formed in the same manner (i.e., they are virtually all primary, or all secondary). Except for rare tourmaline and tremolite crystals, fluid inclusions are the only type of inclusion observed in specimens from non-pegmatitic tin deposits. In view of the ease in which primary inclusions form in artificial minerals, it would

seem most unlikely that in tin deposits primary inclusions never form, but secondary ones are always present.

In some specimens, however, planes of inclusions were observed, which gave filling temperatures considerably lower than the average for the specimen, and the general range found in the study as a whole, and these inclusions probably are secondary. Their distribution is of interest—they are common in quartz and fluorite, but rare in cassiterite, wolframite, topaz and beryl, and were not observed in the specimens of spodumene and amblygonite. In order for secondary inclusions to form, the mineral must be soluble in the enclosed fluid to at least some extent for the cavity to be sealed. As might be expected, the minerals that occur in a wide variety of types of mineral deposits (and are probably soluble under a wide range of conditions), contain these "secondary" inclusions much more commonly than minerals that occur only in restricted geological environments (and are probably only soluble under very restricted conditions).

In Tables I–IV the symbol "P" refers to inclusions that are not distributed in planes and are almost certainly primary. "P(?)" refers to inclusions in planes that are probably primary, "S(?)" to planes of inclusions with abnormally low filling temperatures, which are probably secondary, and "S" to inclusions in planes that cross grain boundaries and are undoubtedly secondary.

DISCUSSION OF RESULTS

Types of Inclusions and their Distribution.—The distribution of the different types of primary or apparently primary inclusions is shown in Table V.

In the distribution of inclusion types, there is a marked difference between most pegmatitic cassiterite and cassiterite from other types of deposits. Although complex or complex(?) inclusions were observed in seven out of

TABLE V

Type of deposit and mineral	No. of spec. examined	Number of specimens containing different types or combinations of types of inclusions								
		H_2O	H_2O–CO_2	H_2O + H_2O–CO_2	H_2O + H_2O–CO_2 (?)	Complex	Complex (?)	Complex + H_2O	Complex (?) + H_2O	Complex + H_2O–CO_2 (?)
Pegmatite										
Cassiterite	10	2		1		4	1	1	1	
Others	13	5	1		1	1		1		1
Normal Vein										
Cassiterite	54	44	1	4	7					
Others	44	36		5	7					
Limestone										
Cassiterite	6	3			3					
Others	2	2								
Bolivian Volcanic										
Cassiterite	5	5								
Others	6	6								
Mexican Volcanic										
Cassiterite	1									

the ten specimens of pegmatitic cassiterite, and are the only type present in five cases, they were not found in any of the specimens from other types of deposits (Cornwall specimens 26, 28, 29 and 31 which have similar inclusions, are of quartz not related to the tin mineralization). H_2O or H_2O-CO_2 inclusions are abundant in all specimens from Normal Vein, Limestone and Bolivian Volcanic deposits, but were observed only in five of the ten specimens of pegmatitic cassiterite, and in only one case could be termed abundant. The obvious conclusion to be made, is that most, but not all, pegmatitic tin deposits form from siliceous melts, but the other types (with the possible exception of the Mexican Volcanic deposits) form from water solutions, which on occasion contain substantial amounts of CO_2.

The similarity of the inclusions in the specimens from Normal Vein, Limestone and Bolivian Volcanic deposits, suggests that these deposits were formed by essentially the same process. It would appear more likely that the mineralogical differences between the Normal Tin Veins and the other types are a result of reactions between the mineralizing solutions and the host rock in the Limestone case, and of abnormally near surface conditions of deposition in the Bolivian Volcanic deposits, rather than a basic difference in the mineralizing fluids.

The inclusion evidence gives little or no support to the application of the term "pneumatotytic" to tin deposits. With one exception, in specimens from Normal Vein, Limestone and Bolivian Volcanic deposits, H_2O inclusions are either the only type present, or by far the most abundant type. In all cases the liquid in these inclusions expanded to fill the cavity at the filling temperature, which indicates that the inclusion formed from a fluid with a specific volume less than the critical volume, and which, as is discussed by Smith (30), would have the properties of a liquid rather than a gas regardless of whether the temperature at the time of formation was above or below the critical temperature. In view of this, these deposits are more properly classified as "hydrothermal" than "pneumatolytic," if the terms are used in the manner suggested by Smith et al. (33). The same argument applies to the pegmatite deposits in which the minerals contain primary H_2O inclusions. Only one possible exception was found. In cassiterite specimen 48, from Graupen, Erzgebirge, only H_2O-CO_2 inclusions are present, and in these the bubbles, which consist of CO_2 gas at room temperature, expand to fill the cavities at the filling temperature. Even in this case, however, the argument for "pneumatolysis" is not conclusive, since a solution of CO_2 gas and liquid water would not necessarily have gaseous rather than liquid properties.

The Mexican Volcanic class of deposits may be truly "pneumatolylic" however, since there is no inclusion evidence to the contrary, and the mineralogical evidence is strongly suggestive of formation under fumarolic conditions.

Filling Temperature Measurements.—The filling temperatures of H_2O-CO_2 inclusions generally have a different significance from those of H_2O inclusions. In the H_2O-CO_2 case the "filling" is a matter of mutual solubility in the two-component system H_2O-CO_2, while with H_2O inclusions the question is usually one of simple liquid-vapour relationships in a one-component system. Be-

cause of this, the well known generalization that filling temperature measurements give a minimum temperature of formation (to which a pressure correction must be added), which is normally applicable to H_2O inclusions, is commonly not justified in the H_2O-CO_2 case.

With H_2O-CO_2 inclusions, as is discussed by Smith and Little (35), a distinction has to be made between minerals that were formed in the presence of only H_2O-CO_2 phase, and those which were formed under conditions of H_2O-CO_2 immiscibility, in which both a H_2O rich and a CO_2 rich phase was present. In the one phase case, as with most H_2O inclusions, the filling temperatures will be *below* the temperature of formation (except in the highly unlikely situation where the H_2O-CO_2 solution was at its exact saturation point). Where two phases were present, however, inclusions that trap either phase will have filling temperatures *equal* to the temperature of formation (with a small, and as shown by Ingerson (14), negligible correction resulting from the compressibility of the host mineral), but those that trap a mixture of the two phases will have filling temperatures *above* the temperature of formation. The distinction between the one-phase and two-phase conditions of formation should normally be a simple matter. If the primary inclusions in a specimen show a relatively constant $H_2O : CO_2$ ratio, the one-phase situation is indicated; if the $H_2O : CO_2$ ratio is highly variable immiscibility was probably the case.

In the present study, only two of the specimens examined meet the requirements of formation in a one-phase H_2O-CO_2 system. In these specimens, only H_2O-CO_2 inclusions were observed, and the $H_2O : CO_2$ ratio in the inclusions, as indicated by the relative size of the CO_2 bubble at room temperature, is constant throughout the specimen. Filling temperatures, as given by the heating stage, are as follows:

TABLE VI

FILLING TEMPERATURE MEASUREMENTS ON SPECIMENS CONTAINING ONLY H_2O–CO_2 INCLUSIONS

Type of deposit	Specimen no.	Mineral	Location	Filling temperature °C	No. of inclusions tested
Pegmatite	22	Beryl	Malaya	334–358	9
Normal Vein	48	Cassiterite	Erzgebirge	361–367	11

With these specimens the filling temperatures can be taken as minimum temperatures of formation, which are subject to a positive correction for pressure, but since no quantitative data are available on P-V-T relations in the system H_2O-CO_2 in the temperature-range in question, it is not possible to make any estimate of the probable magnitude of this correction.

In all of the other specimens in which H_2O-CO_2 or H_2O-CO_2(?) inclusions were observed, they are accompanied by much more abundant "H_2O" type inclusions showing the same general size, shape and distribution. The

TABLE VII

FILLING TEMPERATURE MEASUREMENTS ON SPECIMENS CONTAINING BOTH H_2O AND H_2O–CO_2 INCLUSIONS

Type of deposit	Spec. no.	Mineral	Location	H_2O inclusions		H_2O–CO_2 inclusions	
				Filling temp. °C	No. of inclusions tested	Filling temp. °C	No. of inclusions tested
Pegmatite	23	Cassiterite	Malaya	361	3	366	3
Normal Vein	47	Apatite	Erzgebirge	378–428	8	398	5
Normal Vein	67	Cassiterite	Belgian Congo	358–374	13	378	1
Normal Vein	83	Cassiterite	Belgian Congo	320–386	12	344–350	3
Normal Vein	61	Topaz	Belgian Congo	313–323	14	342–276	5
Normal Vein	129	Cassiterite	Tasmania	280–290	2	334	2
Normal Vein	68	Cassiterite	Belgian Congo	222–252 S?	11	315–375	9
				464–524	18		
Normal Vein	25	Cassiterite	Bolivia	377–387	3	H_2O–CO_2 (?)	
		Quartz		392–398	10	H_2O–CO_2 (?)	
Normal Vein	44	Cassiterite	Cornwall	355–381	3	H_2O–CO_2 (?)	
		Quartz		389–429	8	H_2O–CO_2 (?)	
Normal Vein	50	Topaz	Erzgebirge	295	1	H_2O–CO_2 (?)	
Normal Vein	53	Quartz	Erzgebirge	303–343	12	H_2O–CO_2 (?)	
Normal Vein	62	Quartz	Belgian Congo	334–360	3	H_2O–CO_2	
Normal Vein	66	Quartz	Belgian Congo	337–353	3	H_2O–CO_2	
Normal Vein	110	Cassiterite	Tasmania	270–300	4	H_2O–CO_2 (?)	

filling temperatures of the inclusions in these specimens, as measured with the heating stage, are given in Table VII.

With the "H_2O" inclusions in these specimens, filling occurred in all cases by the *contraction* of the bubble until it disappeared. All of the H_2O-CO_2 inclusions that were tested, however, filled by the *expansion* of the bubble until it filled the cavity. For inclusions with such dissimilar characteristics to show nearly identical filling temperatures, as is the case in the first four specimens, 23, 47, 67 and 83, the only likely explanation is that these minerals were formed in two-phase H_2O-CO_2 systems, and the two types of inclusions represent the H_2O and CO_2 rich phases of these systems. If this is accepted, the filling temperature measurements should represent the temperatures of formation of the minerals almost exactly. The same argument probably also applies to specimens 61 and 110, in which the filling temperatures of the two types of inclusions are fairly similar, and the differences (which are less than the variations shown by the H_2O inclusions in some of the other specimens) can be easily explained by small variations in temperature during the formation of the minerals, or if the H_2O-CO_2 inclusions contain a mixture of the two phases present at the time of formation, rather than only the CO_2 rich one.

In none of these specimens, was it possible to demonstrate that the "H_2O" inclusions contain some CO_2, which would have to be the case if they represent the H_2O rich member of a two-phase H_2O-CO_2 system. It was hoped that cooling, by means of liquid air, would produce observable amounts of an additional phase in the inclusions, but this was not found to be the case. However

this test is by no means conclusive. It is generally only applicable if the concentration of CO_2 is sufficiently high for observable amounts of liquid CO_2 to be present at some stage of the cooling, and there is no necessity that the solubility of CO_2 in water solutions, at the temperatures and pressures under which the minerals formed, is sufficiently high to give this concentration. With lower CO_2 concentrations, even if solid CO_2 formed by sublimation from CO_2 gas present in the bubble of the inclusion, this would occur below the freezing point of the water solution, and it would be most unlikely that the presence of solid CO_2 on the surface of the ice could be recognized. On the whole, the positive evidence for a two-phase system given by the similarity of the filling temperatures of the two types of inclusions, would appear to be much more reliable than the negative evidence of the cooling tests.

For cassiterite specimen *23*, additional evidence for a two-phase system is provided by the inclusions in beryl specimen *22* from the same deposit. The beryl contains only H_2O–CO_2 inclusions that have CO_2 bubbles occupying 47 percent of the cavities at room temperature, and filling in all cases occurred by the contraction of the CO_2 bubble until it disappeared. The cassiterite, however, contains "H_2O" inclusions, with bubbles occupying 30 percent of their cavities; and H_2O-CO_2 inclusions, with CO_2 bubbles varying from 55 to 80 percent of the volume of the cavity. As was mentioned above, the "H_2O" inclusions filled by the contraction of the bubble until it disappeared, but with the H_2O-CO_2 inclusions by the expansion of the CO_2 bubble until it filled the cavity. The only reasonable explanation for the differences between the inclusions in these two specimens, is that the beryl formed in a one phase H_2O-CO_2 system, which had split into two phases, one richer in water, and the other richer in CO_2, by the time the cassiterite was deposited.

For Specimen *68*, however, some other explanation is required for the large difference between the filling temperatures of the different types of inclusions. Either there were large variations in temperature and the composition of the mineralizing solution during the formation of the mineral, or else one or more stages of secondary inclusion formation occurred. Because of this, the filling temperature measurements on this specimen cannot be used to determine the temperature of formation.

For the remaining specimens listed in Table VII, filling temperature measurements were made only on "H_2O" inclusions, and in most cases the H_2O-CO_2 inclusions were not even positively identified as such. While it is by no means certain that with these specimens the filling temperatures represent the temperatures of formation, this is a definite possibility, and it is interesting to note that in all cases the filling temperatures are in the same range (roughly 300–400° C) given by specimens *23*, *47*, *67* and *83*, for which the relationship between filling temperatures and temperatures of formation can be considered as being well established.

The filling temperature measurements obtained from specimens containing only H_2O inclusions are listed in Table VIII.

These filling temperatures can be considered as minimum temperatures of formation, which are subject to positive corrections for the pressure at the

TABLE VIII

FILLING TEMPERATURE MEASUREMENTS ON SPECIMENS CONTAINING ONLY H_2O INCLUSIONS

Type of deposit	Spec. no.	Mineral	Location	Filling temperature	No. of inclusions tested
Pegmatite	17	Spodumene	Belgian Congo	220–272	11
	20	Amblygonite	Belgian Congo	305–321	3
Normal Vein	24	Cassiterite	Bolivia	336–356	8
	38	Fluorite	Cornwall	240–264 S(?)	9
				391–405	5
	40	Cassiterite	Cornwall	388	3
				484–514	10
	49	Cassiterite	Erzgebirge	401–411	5
	54	Cassiterite	Spain	308–322	4
	55	Cassiterite	Portugal	280	1
	63	Cassiterite	Belgian Congo	184–204 S(?)	3
				334	1
	64	Cassiterite	Belgian Congo	270–288	2
	65	Cassiterite	Belgian Congo	236–252	4
	70	Cassiterite	Belgian Congo	405–437	4
	75	Topaz	Belgian Congo	381	1
	76	Cassiterite	Belgian Congo	289	1
	79	Cassiterite	Belgian Congo	348–358	8
	80	Cassiterite	Belgian Congo	160 ???	1
	84	Cassiterite	Belgian Congo	387	1
	87	Cassiterite	Belgian Congo	349–355	12
	88	Quartz	Belgian Congo	280–340	8
	90	Cassiterite	Belgian Congo	344–360	4
	98	Cassiterite	Billiton	184–194	2
	99	Quartz	Billiton	224–232	8
	100	Fluorite	Billiton	80	3
	106	Quartz	Tasmania	248–268 S?	5
				394–416	4
	111	Scheelite	Tasmania	145–151	4
	112	Fluorite	Tasmania	146–154	11
	113	Quartz	Tasmania	291	1
Limestone	116	Cassiterite	Alaska	334–344	2
Bolivian Volcanic	123	Quartz	Llallagna	376–382	6
	124	Quartz	Llallagna	330–360	4
	126	Cassiterite	Llallagna	394–406	5
	128	Apatite	Llallagna	295–301	11

time of formation. Although the "pressure corrections" cannot be calculated without accurate information on the pressure of formation, the chemical composition of the solutions in the inclusions, and quantitative P-V-T data on such solutions (none of which is available), a fairly reliable estimate of the probable range of these corrections can be made, and is given in Table IX.

The depths of formation given in this table are very approximate, but would appear to be geologically reasonable. The pegmatites are mostly in areas of high regional metamorphism, which is suggestive of a deep-seated origin. The Normal Vein and Limestone deposits are commonly in areas of fairly low *regional* metamorphism, and their vuggy nature, and short vertical extent point to fairly shallow depths of formation. Shallower depths could

be expected for the Bolivian Volcanic deposits, because of their lack of associated granites and extreme mineralogical zoning. The pressure figures are the rock load equivalents of the depths of formation given by Smith (30a). P-V-T data for pure water (16) were used in calculating the corrections for pressure, the assumption being made that for a given pressure of formation, the correction applicable to an inclusion containing a water solution of unknown composition, will be the same as the correction that is calculated for a hypothetical inclusion containing pure water but having the same volume of cavity : volume of liquid ratio (i.e., approximately the same specific volume). The maximum and minimum correction figures result from combining the maximum and minimum cavity : liquid ratios of observed inclusions with the maximum and minimum pressure figures.

TABLE IX

RANGE OF PRESSURE CORRECTIONS, FOR FILLING TEMPERATURE MEASUREMENTS ON SPECIMENS CONTAINING ONLY H_2O INCLUSIONS

Type of deposit	Depth of formation (miles)	Pressure (bars)	Vol. inclusion / Vol. liquid	Pressure corr. (° C)
Pegmatite	4–10	1,700–4,250	1.24	100–300°
Normal Vein, Limestone	2–4	800–1,700	1.23–1.35	60–130°
Bolivian Volcanic	½–2	250–800	1.25–1.41	10–70°

Applying these pressure corrections to the filling temperatures given in Table VIII, gives temperatures of formation which are mostly in the 300–500° C range. This result is independent of whether the maximum or minimum pressure corrections are used, and also would not be changed if the figures for these corrections are as much as 50 percent in error. Cassiterite specimen 40, from Cornwall, appears to have formed at a temperature above 500° C, and this may be the case with a number of other specimens if relatively large pressure corrections are applicable. There are no clear cut examples of tin mineralization occurring at temperatures below 300° C. Although a filling temperature of 160° C was obtained from cassiterite specimen 80, from the Belgian Congo, this value is very questionable, since only one inclusion was tested, and the estimated filling temperatures of other inclusions in the specimen are considerably higher. Cassiterite specimen 98 and quartz specimen 99, from the Klappa Kampit Mine, Billiton, gave fairly low filling temperatures (189 ± 5 and 228 ± 4° C), but the exceptional depth continuity of this deposit suggests that it may have formed at a greater depth than is usual for Normal Tin Veins, and abnormally large pressure corrections may be applicable. Scheelite specimen 111 and fluorite specimen 112 from the Aberfoyle Mine, Tasmania, gave filling temperatures of approximately 150° C, but these minerals probably represent a late stage of the mineralization since cassiterite (specimen 110) and quartz (specimen 113) from the same deposit gave filling temperatures of 285 and 291° C, and the calculated filling temperature for the inclusions in wolframite (specimen 113) is 280 ± 30° C. The

same explanation probably applies to the very low (80° C) filling temperature obtained from Billiton fluorite specimen no. 100.

The use of filling temperature measurements on fluid inclusions in geothermometry carries the inherent assumption that there has been no significant leakage of fluid, either into or out of the inclusions, since they were formed. Widely different views have been expressed on the validity of this assumption (17, 33, 25, 32, 21), experimental work carried out to investigate this problem (25, 21) has produced conflicting results, and there are conflicting opinions as to how the experimental results should be interpreted in terms of geological conditions.

In the present study, no evidence was found for the leakage of inclusions, and in general the results suggest that it rarely, if ever, occurs. The cases in which both H_2O and H_2O-CO_2 inclusions, having nearly identical filling temperatures, were found in the same specimen, are almost impossible to explain if leakage has taken place. Because of the very large difference between the contents of the two inclusion types, they would have to leak to a considerably different degree for the identity of the filling temperatures to be maintained or produced, and it would seem to be a remarkable coincidence that this differential leakage should occur in just the exact amount necessary to give filling temperature identity. The general similarity of the filling temperatures obtained from all the specimens of cassiterite and associated minerals, suggests that either leakage always occurs (which seems unlikely), or that it is rarely an important factor.

Kennedy, one of the main exponents of inclusion leakage, has suggested (17) that the only practical way to tell whether or not it has occurred, is to decide whether or not the temperatures of formation obtained from filling temperature measurements are geologically reasonable. If this criteria is accepted, the results of the present study provide strong evidence against the importance of leakage. A temperature of formation range of 300–500° C fits in with generally accepted ideas that tin mineralization is restricted to high temperatures (as is indicated by the close proximity of most tin deposits to granite bodies, and the presence of skarn type silicates in most (if not all) tin deposits in limestone) with an upper limit of approximately 600° (set by low to high quartz relationships and Goranson's (6) experimental data on the melting point of granite.)

Chemistry of Tin Transportation.—Although chemical analysis of the contents of primary inclusions, which provides a direct method for studying the chemistry of tin transportation, was beyond the scope of the present study, some of the observations of a more general nature can be used to assess methods of transportation that have been proposed.

The suggestion by Daubrée (4) that tin is transported in the gaseous state as $SnCl_4$ or SnF_4, has had wide acceptance, and is supported by the common occurrence of fluorine bearing minerals in tin deposits, and by experimental work of St.-Claire Deville (40), who produced artificial cassiterite from $SnCl_4$ gas. However it has not been demonstrated that $SnCl_4$ or SnF_4 are stable in the presence of water under conditions that are geologically likely—

under most conditions they are highly unstable in the presence of water. The inclusion data, which indicates either siliceous melts, or aqueous solutions with liquid rather than gaseous properties, does not favour this process. It may apply, however, to the Mexican Volcanic deposits, for which inclusion data is lacking, and the geological and mineralogical evidence suggests fumarolic conditions of deposition.

More in accordance with the inclusion data, are suggested methods of tin transportation that involve tin compounds soluble in aqueous solutions. The possibility of tin being transported as an alkali stannate, as suggested by Simmons (*23, 24*) or as an alkali thio-stannate, was demonstrated by Smith (*27*) by the preparation of artificial cassiterite from such solutions. The alkali thio-stannate method is particularly adaptable to the tin deposits that are high in sulphides (such as the Bolivian Volcanic type).

An additional possibility, which apparently has not been considered previously, is transportation in alkali fluo- or chloro-stannate solutions. Fluo-stannate transportation might be the explanation of the common association of fluorine bearing minerals with cassiterite. Although there has been no experimental work to show that cassiterite can be deposited from such solutions, the following solubility data (2, pp. 490, 492) are of considerable interest:

SOLUBILITY IN GMS PER 100 ML

	Cold water	Hot water
K_2SnF_6–H_2O	3.7 (18° C)	33.3 (100° C)
K_2SnCl_6	Soluble	Soluble

CONCLUSIONS

1. From the inclusions in cassiterite and associated minerals, it would appear that most, but not all, pegmatitic tin deposits have been formed from siliceous melts, but that the remaining pegmatites and all other types of tin deposits (with the possible exception of the Mexican Volcanic class), have been formed from water solutions. Since under the conditions of deposition, these water solutions had the properties of liquids rather than gases, the deposits are more properly classified as "hydrothermal" than "pneumatolylic."

2. Filling temperature measurements indicate that most hydrothermal tin deposition occurs in the 300–500° C range, although the temperature may be as high as 600° C.

3. Of the previously suggested methods of tin transportation, alkali-stannate and alkali thio-stannate solutions are in accordance with the inclusion data. Additional possibilities are alkali chloro- and fluo-stannate solutions.

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SULFUR ISOTOPE FRACTIONATION IN SULFIDE MINERALIZATION

S. GAVELIN, A. PARWEL, AND R. RYHAGE

ABSTRACT

The isotopic compositions of sulfides and sulfates from various types of sulfide formations have been determined. A description of the preparation of sulfurous minerals for mass-spectrometric analysis and of the mass-spectrometric procedure is given.

The results agree in several respects with previous investigations. Various sulfides representing a continuous mineralization process display no significant divergencies if the early and the late minerals are compared. Nor does the material examined indicate any correlation between isotopic composition and zonal arrangement of minerals and metals around emanative centers, in cases where such zoning is evidenced by the regional geological features. A certain correlation between kind of wall-rock and isotopic composition may be indicated. If considerable variations of isotopic compositions are found to exist in an ore district, the range of variation seems to be wider in the low-temperature than in the high-temperature sulfides.

Supergene oxidation of sulfides to sulfates takes place without change in isotopic composition. A subsequent redeposition of supergene sulfides may involve a displacement of the isotope ratios towards lighter sulfur.

Hypogene sulfide mineralization, where both sulfides and sulfates are formed, is apt to cause significant fractionation of the original isotopic composition of the participant sulfur. Local variations indicate that the process may develop differently over short distances. The local character of some isotope exchange reactions is evidenced for instance by considerable variation in the isotope ratios even in a single hand specimen. The range of such variations is generally found to be wider in low-temperature than in high-temperature mineral assemblages.

INTRODUCTION

THE fact that sulfur from various sources in nature exhibits slight variations in isotopic composition has in recent years given rise to extensive research work. In this connection the relative abundances of sulfur isotopes in various sulfide ore deposits have also been studied in order to elucidate their genesis. In the present paper some results are presented that might be of more general interest in this respect. They form part of a broader investigation started some years ago in which the material was partly chosen to permit examination of the sulfur isotope composition in Swedish sulfide ores and partly for the study of such factors, as whether supergene oxidation and re-deposition of sulfides or zoning can be correlated with any kind of significant isotope fractionation.

Up to now some 300 samples have been analyzed. The preparation of the sulfides for mass-spectrometric analyses was performed at the Mineralogi-

cal Department of the Swedish Museum of Natural History, Stockholm, under the guidance of A. Parwel. The mass-spectrometric measurements were carried out at the Chemical Department, Karolinska Institutet, Stockholm, by R. Ryhage.

Chemical Preparation of the Samples.—Sulfur dioxide was used for the mass-spectrometric measurements. Because the chemical preparations were made in one laboratory and the mass-spectrometric measurements in another, situated elsewhere in Stockholm, it was imperative to have a simple reliable method to prepare sulfur dioxide in the mass-spectrometric laboratory.

The procedure finally selected consisted of quantitatively converting the sulfur of all samples into CdS, which intimately mixed with V_2O_5 in the molecular proportions 1:3 was heated to 600° C, giving 95–96 percent of the sulfur present as SO_2. The reasons for choosing CdS are: CdS and 2nS are both particularly resistant to oxidation when precipitated from a solution, the former being more resistant than the latter; it is also easier to precipitate and filter. V_2O_5 was chosen as oxidizing agent because it gave the most satisfactory results and it is easy to keep in stock in large quantities. This ensures the same oxygen over long periods of time for sulfur isotope determinations.

A cadmium sulfide of "purum" quality is used as an internal standard. After drying at 400° C in an oxygen-free stream of nitrogen it contained 99.1% CdS.

Commercial V_2O_5 always contains CO_2, nitrogen compounds, commonly chlorine compounds, and small amounts of SO_3. The V_2O_5 used was purified therefore by heating it for about 75 hours at 620–640° C, in order to drive off all gaseous compounds (CO_2, NO, Cl_2, SO_3, etc.), that may be liberated at 600° C. The product was still in powder form and was tested mass-spectrometrically. Small amounts of CO_2 and NO without importance for the measurements were detected but sulfur was no longer detectable.

In the preparation of CdS the first step was to convert the sulfur-containing material into a suitable sulfide. Sulfates, as for example $BaSO_4$, were well mixed with an excess of carbonyl iron (contains about 0.003% S) and zinc powder. The latter was used in order to accelerate the reducing reaction; alone it is unsuitable as the reaction proceeds too rapidly. A mixture of 5×10^{-3} mol of sulfate with 4.5 gm carbonyl iron and 0.5 gm of zinc powder was used in the first stage of a preparation. The mixture was placed in a porcelain crucible and covered with a carbonyl iron layer. The crucible, covered with a lid was heated with a blaster for 30 min. For $BaSO_4$ the temperature was kept at about 950° C, for $SrSO_4$ at about 820° C and for $CaSO_4$ at about 750° C.

Samples containing As, Sb, Sn, and similar elements or only small amounts of sulfur were oxidized to SO_4 and the sulfur was precipitated as $BaSO_4$, which was treated as above. Samples containing elemental sulfur, pyrite, or sulfosalts were mixed with carbonyl iron and heated in a porcelain crucible at 700° C for about 10 minutes.

The porcelain crucible, which never contained more than 5 millimol of sulfide, was placed in an apparatus with standard joint connections. Air was

replaced by blowing oxygen-free hydrogen through the apparatus for about 60 minutes. Hydrochloric acid (10%) was added and the liberated H_2S absorbed in two absorption flasks. In the first flask 300 ml of a solution was placed containing 5% HCOOH and 0.75% $Cd(HCOO)_2$. In the second flask there were 75 ml of 1.5% neutral $Cd(HCOO)_2$ solution. The second absorption flask was used in order to ensure complete absorption of H_2S. The temperature in the first flask was kept at 95–100° C during the process in order to obtain CdS in as crystalline a condition as possible. When the reaction was complete, all H_2S was blown into the absorption flask by means of hydrogen. The content of the second absorption flask was poured into the first flask and then filtered through a Jena G4 glass filter. The CdS was washed 7 times with a 3% HCOOH solution, 3 times with 95% C_2H_5OH, and then dried at 100–110° C. The dry CdS was pulverized and dried once more in an oxygen-free nitrogen stream at 400–425° C. It was necessary to dry at 400° C in order to decompose possible $Cd(HCOO)_2$ and $CdCO_3$ (decomposition temperature 358° C) present.

For the measurement in the mass spectrometer 1 part CdS and 4 parts V_2O_5 were mixed; 0.1 gm of this mixture was placed in a tube of pyrex glass about 150 mm in length and 10 mm in diameter and fitted with standard joints. This tube was connected directly to the mass spectrometer and then heated continuously with a bunsen flame to about 600° C. Liberated SO_2 was used in the determination of the sulfur isotopes.

Mass Spectrometer Measurements. The mass spectrometer used was a 180° type instrument (21). By using the double collector and the null method, described by Nier (12), the measurement were carried out on the SO_2^+-ions with mass numbers 64 and 66.

The pressure of SO_2 gas in the intake system was regulated so that the $m/e = 64$ ion current gave an output voltage on the d.c. amplifier of about 20 volts.

A galvanometer served as balance indicator; in the sensitivity range used 0.05 percent of the M66/M64 ratio of standard SO_2 corresponds to a 5 mm galvanometer deflection. By using the double collector method alternately on the standard gas and on samples, any changes relative to the standard gas in the abundance of the samples were determinable.

The precision of the instrument, when used on isotopic abundances of SO_2, is about $\pm$ 1‰. About 10 minutes was needed to analyze one sample. Isotopic fractionation of the heated samples did not occur. This was determined by repeating the heating and measuring procedure three times for some samples. In these cases the isotopic abundances were not found to change.

PREVIOUS WORK AND SOME GENERAL CONSIDERATIONS

A Canadian research group [Macnamara (9, 10, 11), Szabo (15), Thode (16, 17, 18, 19), Tudge (20) and others] was first to show that significant variations of isotopic composition do exist in natural sulfur of various origins. They were also able to demonstrate that the variations found empirically were in agreement with those that could be expected from calculated equilib-

rium constants for certain isotopic exchange reactions that can be assumed to play a part in geological processes. Particularly processes involving the oxidation-reduction of sulfur compounds were found to represent a mechanism by which fractionation of the sulfur isotopes may take place in nature.

The Canadian group presented several determinations on sulfur from various ore deposits but it did not enter into details on the bearing of sulfur isotope fractionation to genetic problems of sulfide ores. These problems have subsequently been discussed by several authors, for instance, Kulp, Ault, and Feely (8), Bateman and Jensen (2), Jensen (7), Vinogradow, Cupachin, and Grinenko (22), and Sakai (14). In several of these articles surface oxidation-reduction processes of sulfur compounds were tentatively postulated as an explanation of variations in isotopic compositions in the material examined. Although this is probably not the only mechanism by which significant isotope fractionation can be realized in nature, the results presented by the Canadian group suggest the matter to be worth close attention. Oxidation-reduction reactions certainly also take place in many geological processes at higher temperatures but for the problem in consideration it is important to remember that isotope fractionation is much less at high than at low temperatures. Tudge and Thode (20) worked out the equilibrium constants of several reactions at 0° and 25° C and recently Sakai (14) extended the calculations to cover a range of temperature from 0 to 1,000° C. From Sakai's diagram it is clear that if the exchange reactions calculated by him are actually realized, the fractionation of the sulfur isotopes must be more extensive under exogenic than under magmatic and hydrothermal conditions. This fact would offer a chance of tracing prior exogenic processes in material that has subsequently passed through stages of high-temperature transformations. In a later paragraph this problem will be discussed further with regard to some of the results presented in the present paper.

PRESENTATION OF THE ANALYSES OF THE PRESENT INVESTIGATIONS

The results were calculated as ‰ -deviation (δ) from a standard (in this case cadmium sulfide) according to the formula

$$\delta\,{}^{0}/_{00} = \frac{S^{34}/S^{32}\ (\text{sample}) - S^{34}/S^{32}\ (\text{standard})}{S^{34}/S^{32}\ (\text{standard})} \times 1{,}000.$$

Material of sulfide ore from Sudbury, Ontario, made it possible to calibrate our standard with that of the Canadian research group. According to information from Dr. Monster, their meteorite standard is assumed to be $S^{32}/S^{34} = 22.225$, and for the nickel sulfide standard used for calibration it is $S^{32}/S^{34} = 22.203$. The δ-values in the present article are given as the deviations from the meteorite standard of the Canadian research group and are, therefore, comparable to all published sulfur isotopic studies. The arithmetical mean of 22 separate analyses of the Canadian nickel sulfide standard showed the Stockholm standard to be $\delta = +2.19$, with a standard deviation of ± 0.68. Consideration of the entire number of analyses, where several

determinations on the same sulfide mineral in a sample were performed, indicates that the results can be reproduced with a standard deviation of ± 0.7–0.8‰, when only one analysis is performed on a sample. Several samples, especially those displaying peculiar or unexpected values, were checked by several analyses and therefore must have a higher degree of precision.

A summary of the analyses to be considered in the present paper is given in Figure 1. The results are grouped as answers to the following questions: 1. Are there any significant variations in the isotopic composition of sulfur from sulfides representing various stages of sulfide precipitation in a continuous mineralization process? 2. Does any correlation exist between the spatial zonal distribution of various metals occurring in many ore districts and isotopic composition of sulfur from these same metal zones? 3. Does any isotope fractionation of sulfur occur when sulfide minerals are oxidized and when new sulfides are precipitated in connection with weathering? 4. Do co-existing "primary" sulfide-sulfate minerals in ore veins indicate any isotopic fractionation during hypogene mineralization. 5. How are considerable variations in isotopic composition of sulfur from sulfides within a very small amount of material (for instance in one hand specimen) to be interpreted? Some of these questions have already been considered by the authors cited above and the results of the present paper may therefore in some cases serve mainly as a complement to the empirical data on the subject.

RELATIVE ISOTOPE ABUNDANCES IN SULFUR FROM VARIOUS STAGES IN A CONTINUOUS SULFIDE MINERALIZATION

Two Swedish ore deposits (Table 1) were chosen to represent this part of the investigation, Boliden and Falun, the geology of which have been described by Ödman (13) and Geijer (5). In both these deposits the main ore bodies form fairly compact masses of pyrite with subordinate quantities of pyrrhotite, arsenopyrite, chalcopyrite, sphalerite and galena. In both cases the sulfide mineralization is associated with an intense alteration of the wall rocks (in Boliden mainly quartz-sericite- and/or chlorite-schists, in Falun cordierite-anthophyllite-quartz-schists and skarn rocks). Ödman in his study of the Boliden deposit was able to establish that the sulfide mineralization took place in three stages; the first characterized by the formation of dense masses of arsenopyrite, the second by a multitude of complex minerals containing antimony, selenium, tellurium, bismuth and gold, commonly associated with quartz-tourmaline veins and lamprophyre dikes; the third stage comprises the formation of large masses of pyrite. In all three stages certain amounts of pyrrhotite, chalcopyrite, sphalerite and galena were also formed. In Figure 1 the three stages are denoted by the numbers 1, 2 and 3. One of the chalcopyrite samples and also the pyrrhotite specimen analyzed cannot be assigned to any of the three stages (under n.d. in Fig. 1). The range of variation of the 8 values from Boliden covers only about 2‰ and no difference between sulfur from the various stages of mineralization can be discerned. The seven values representing various sulfide minerals from Falun show approximately the same variations. They certainly represent a fairly wide

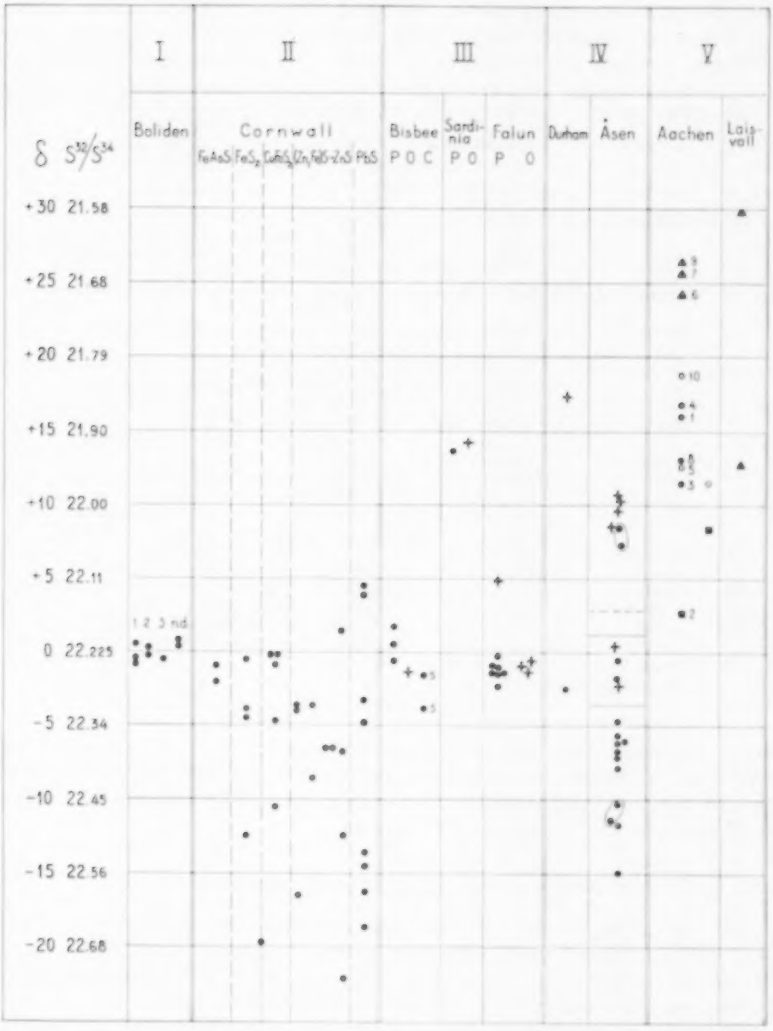

FIG. 1. Survey of isotopic composition of samples analyzed. In columns I, II, III, IV the circles refer to sulfide minerals and the crosses to sulfates. In column V: square = galena; filled circle = brown sphalerite; open circle = yellow sphalerite; triangle = pyrite.

TABLE 1

SULFIDES AND SULFATES FROM THE BOLIDEN AND FALUN MINES, SWEDEN

Analysis no.	Mineral	Locality	Type of ore or rock	δ
16	Arsenopyrite	Boliden Mine	Dense compact arsenopyrite ore (first stage of mineralization)	−0.9
17	Chalcopyrite	Boliden Mine (from the same specimen as no. 16)	Dense compact arsenopyrite ore (first stage of mineralization)	−0.6
18	Arsenopyrite	Boliden Mine	Dense compact arsenopyrite ore (first stage of mineralization)	+0.6
22	Selenocosalite	Boliden Mine	Quartz-tourmaline ore (second stage of mineralization)	−0.3
23	Selenocobellite	Boliden Mine	Quartz-tourmaline ore (second stage of mineralization)	−0.2
19	Pyrite	Boliden Mine	Compact pyrite ore (third stage of mineralization)	−0.6
20	Chalcopyrite	Boliden Mine	Chalcopyrite-quartz-vein (not defined as regards stage of mineralization)	+0.3
21	Pyrrhotite	Boliden Mine	Compact pyrrhotite ore (not defined as regards stage of mineralization)	+0.8
12	Pyrite	Falun Mine	Compact pyrite ore	−0.9
13	Pyrite	Falun Mine	Compact pyrite ore with chalcopyrite	−1.0
14	Pyrite	Falun Mine	Compact pyrite ore	−1.4
15	Chalcopyrite	Falun Mine	Compact pyrite ore with chalcopyrite (from the same specimen as no. 13)	−2.3
24	Sphalerite	Falun Mine	Compact pyrite-sphalerite ore	−0.2
25	Galena	Falun Mine	Compact pyrite-sphalerite-galena ore	−1.3
209	Galena	Falun Mine	Compact pyrite-sphalerite-galena ore	−1.3
5	Anhydrite	Falun Mine	In lime-silicate rocks	+7.1
11	"Vitriol"	Falun Mine	"Weathering coatings" on ore	−1.2
210	"Vitriol"	Falun Mine	"Stalaktites" in ore tunnel	−0.9
220	Sulfate from mine water	Falun Mine		−0.6

range of crystallization temperature, pyrite being the first, and galena the last sulfide to crystallize during mineralization. Consequently it can be stated that no significant sulfur isotope fractionation occurred during the mineralization process in the two examples mentioned.

MINERAL ZONING AND SULFUR ISOTOPE COMPOSITION

A zonal arrangement of ore minerals and metals around emanative centers is a well-known feature in many ore districts. Though there still exists a certain divergency as far as the ideas of the ultimate cause of this phenomena is concerned it must be regarded as a fact proved by experience. For an examination of an eventual correlation between mineral zones in that respect and isotope composition of the sulfides the Cornwall district was chosen. The geology of this ore district hardly needs any particular presentation in this connection—a comprehensive monograph of the various deposits was recently published by Dines (3), which also gives a survey of previous publications on the district. Stannite and wolframite form characteristic minerals of the

zone closest to the emanative center; first copper sulfides and arsenopyrite follow outwards, then sphalerite and galena and finally antimonite. The first set of specimens examined was divided by Dines into three groups, representing veins characterized as high temperature, intermediate temperature, and low-temperature formation. In consideration of the experience from the Swedish sulfide ore districts and since the veins of the Cornwall district are generally considered to represent a very well-defined mineralization in space and time it would be expected that the sulfur isotope composition would display fairly small variations. The results as presented in Table 2 and Figure 1 are therefore surprising in this respect, the range of variation being remarkably wide. The very extreme value, $\delta = 50.3$ ($S^{32}/S^{34} = 23.41$) has been excluded in Figure 1, since it refers to a specimen with colloform sphalerite, which may have been formed under somewhat different conditions as

TABLE 2

SULFIDES FROM THE CORNWALL DISTRICT

Analysis no.	Mineral	Locality	Characteristics of specimen	δ
		St. Just District		
33	Chalcopyrite	Geever Mine		−0.1
		Gwinear District		
150	Chalcopyrite	Treasury		−0.9
		Mount's Bay District		
149	Galena	Huel Penrose		−3.2
		Camborne Redruth and St. Bay District		
32	Arsenopyrite	South Croft Mine	Arsenopyrite in quartz and chlorite	−0.9
37	Pyrite	South Croft Mine	Pyrite coatings on fluorite	−0.5
		St. Agnes District		
26	Galena	South St. George Mine (Lambriggan)	Coarse-crystalline galena	−5.9
29	Sphalerite	Lambriggan Mine	Yellow sphalerite and chalcopyrite	−6.5
31	Sphalerite	Lambriggan Mine	Yellow sphalerite and chalcopyrite	−6.5
153	Sphalerite	Great South Chiverton	Yellow sphalerite	−12.4
155	Sphalerite	Goonhavern	Brown sphalerite	−8.5
		St. Austell District		
162	Sphalerite	Wheal Ding (Bodmin Wheal Mary)	Yellow-brown sphalerite	−6.8
		Wadebridge District		
160	Sphalerite	Pengenna	Brown sphalerite	−3.6
		Liskeard District		
156	Sphalerite	South Caradon	Colloform yellow sphalerite	−50.3
163	Galena	Menheniot		−14.5
159	Sphalerite	Penhawger	Dark brown sphalerite with some galena and pyrite	−3.6
146	Arsenopyrite	Treburland		−2.0

TABLE 2—(*Continued*)

Analysis no.	Mineral	Locality	Characteristics of specimen	δ
		Callington and Tavistock District		
147	Galena	Holmbush		−16.2
157a	Chalcopyrite	South Crebor (New East Russel)	Chalcopyrite and dark sphalerite	−4.7
157b	Sphalerite	South Crebor (New East Russel)	The same specimen as no. 157a	−3.9
158	Galena	Devon and Courtney		−13.5
154	Pyrite	Capunda	Pyrite with dark sphalerite and galena	−4.3
35	Pyrite	Collacombe Mine	Pyrite in quartz	−3.9
34	Chalcopyrite	Betsy Mine	Fine-grained chalcopyrite and pyrite in quartz	−19.8
38	Sphalerite	Betsy Mine	Coarse-grained dark sphalerite in quartz	−16.5
		Dartmoor and Teign District		
36	Pyrite	Bulkamore Mine	Fine-grained pyrite with quartz and chlorite	−12.5
161	Chalcopyrite	Queen of the Dart		−10.5
151	Sphalerite	Silver Brook	Yellow-brown sphalerite	−22.3
30	Galena	Exmouth Mine	Galena with barite	−18.8
		North Devon and West Somerset District		
148	Sphalerite	Combe	Yellow-brown sphalerite	+1.5
28	Chalcopyrite	Brimley Mine (Molland)		−0.1
27	Galena	Knap Down (Combe Martin)	Fine-grained galena with quartz	+3.9
152	Galena	Combe Martin		+0.1

compared with the other sulfides from the Cornwall region. The sulfur of this sphalerite has the highest S^{32}/S^{34}-ratio of sulfur from natural sources yet reported in the literature.

In Table 2 the specimens analyzed are grouped with respect to the mining districts as presented in the monograph of Dines (op. cit.) and in the same order as given by him, i.e., in the main from south-west towards the east and the north. In Figure 1 the analyses are grouped with respect to the sulfide mineral examined. The sphalerite samples have been divided into several groups with respect to varying color, i.e., iron content—in the table denoted by ZnS (= iron-poor sphalerite) → (Zn, Fe)S (= iron-rich sphalerite).

If the various minerals are first compared (Fig. 1) it is seen that there does not seem to be any consistent difference between various mineral species as regards their sulfur isotope composition. The material examined, at least, does not permit any statement as to there being significant differences between the average values of the various minerals; therefore, the wide range of variation within the entire material from the Cornwall District cannot have been caused by a characteristic isotope composition in the various sulfide species. It can possibly be stated that the range of variation is particularly wide in galena and light-yellow sphalerite as compared with the other sul-

fides. However, as the various sulfide minerals are represented by a different number of analyses, a more definite statement can hardly be made.

Table 3 is a survey of sulfide isotope determinations of those samples that where grouped by Dines to represent various temperature zones of mineralization. Of course a grouping of this kind only suggests that the mineralization process took place mainly under conditions of high temperature or low temperature respectively, and not that the range of crystallization temperatures characteristic of the various zones could not overlap somewhat.

As a matter of principle the results indicate the same kinds of variations as were found by comparing the various sulfide minerals: Consistent and regular changes from high-temperature to low-temperature zones do not seem to exist but the range of variation appears to be wider in the lower-temperature than in the higher-temperature zones. This impression is at least in part strengthened by the determinations from the Cornwall District, not included in Table 3. At least two values representing the high-temperature

TABLE 3

SULFIDES FROM VARIOUS TEMPERATURE ZONES OF THE CORNWALL DISTRICT

	Analysis no.	δ
High-temperature zone	32	−0.9
High-temperature zone	33	−0.1
High-temperature zone	37	−0.5
Intermediate-temperature zone	28	−0.1
Intermediate-temperature zone	35	−4.9
Intermediate-temperature–low-temperature zone	34	−16.5
	38	−19.8
Low-temperature zone	27	−4.9
Low-temperature zone	28	+3.9
Low-temperature zone	29	−6.5
Low-temperature zone	30	−18.8
Low-temperature zone	31	−6.5
	36	−12.5

zone may be added (on account of mineral assemblage and position in the field): No. 146 with $\delta = -2.0$ and No. 149 with $\delta = -3.2$. Some of the most extreme light-sulfur values from the district are also found in specimens which for the same reasons as mentioned above must be assumed to represent the low-temperature zone. Nevertheless distinct light-sulfur also occurs in sulfides that would represent high- or intermediate-temperature zones. A correlation between mineral zoning around emanative centers and sulfur isotope composition is therefore not indicated in the material here studied.

A study of the regional distribution of the samples analyzed reveals that the isotope compositions of the Cornwall sulfides do not vary altogether at random. If more than one specimen is analyzed from one locality the results are found to be similar and often the same holds true for specimens from adjacent localities. Figure 2 gives a survey of the positions of the samples analyzed. All samples from the northern region (adjacent to the Bristol Channel) and all samples from the south-western regions are characterized by values in the heavy-sulfur portion of the Cornwall group. These areas

represent the inner parts of the Devonian rock complex. The samples from the Carboniferous areas are characterized by light sulfur. In the areas between the Carboniferous sequence and the Devonian rocks of the western portion of the Cornwall peninsula are many intermediate values; there are,

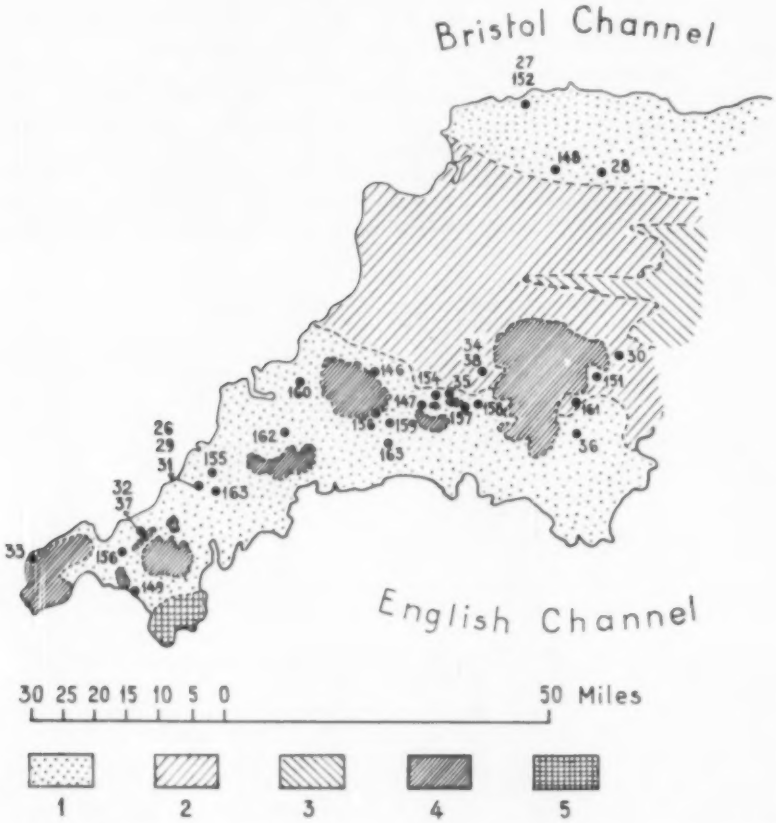

FIG. 2. Geologic sketch map of the Cornwall District and positions of the samples analyzed. The figures represent the designation numbers of the analyses. 1. Devonian; 2. Carboniferous; 3. Permian; 4. Granite; 5. Basic intrusions.

however, great variations towards both the heavy-sulfur and the light-sulfur side of the range of variation characteristic of the entire material from the Cornwall area. The significance of these results will be discussed in a later section of this paper.

SULFATES AND SULFIDES FORMED DURING THE OXIDATION OF SULFIDE DEPOSITS

Some analyses of sulfides and sulfates are presented in Table 4 and Figure 1, column III, which are intended to demonstrate the variation of the isotope ratios in the oxidation of "primary" sulfides. The primary sulfides are grouped under column P in figure 1, sulfides formed by exogene oxidation under column O (brochantite from Bisbee, anglesite, grown on galena crystals, from Sardinia, and hydrous copper-, zinc, or iron-sulfates ("vitriol") from Falun [1]. As is readily seen, the sulfide and sulfate values do not display significant differences, which means that the oxidation in these cases must have been a unidirectional process. The results are in full agreement with those found by Sakai (14) and Ault (1). The specimens from Bisbee and Sardinia are from collections in the Mineralogical Institute, University of Stockholm, and the present author has no personal experience of their field relations. The field data of the Falun mine, however, are well-known to

TABLE 4

RELATION BETWEEN SULFATES AND SULFIDES FORMED BY SUPERGENE OXIDATION OF PRIMARY SULFIDES

Analysis no.	Mineral	Locality	Characteristics of specimen	δ
212	Chalcopyrite	Campbell Mine, Bisbee	Compact chalcopyrite ore	+1.8
213	Pyrite	Campbell Mine, Bisbee, Center of orebody	Coarse-crystalline pyrite	+0.6
216	Pyrite	Campbell Mine, Bisbee	Fine-grained pyrite impregnation in porphyry	−0.6
219	Brochantite	Campbell Mine, Bisbee	Compact brochantite mass	−1.3
214	Chalcocite	Sacramento Hill, Bisbee	Compact sulfide mass	−1.7
215	Covellite	Sacramento Hill, (pocket in open pit)	Compact sulfide mass	−3.9
217	Anglesite	Sardinia	Crystals on galena	+14.4
218	Galena	Sardinia	The same specimen as no. 217	+13.6

the writer and are of a certain interest in the present case. The mine has been operated for at least 700 years and the walls of the open pits have collapsed on several occasions during that period. Masses of large blocks still occur therefore in the upper part of the mine. This means that these upper parts are intensely penetrated by aereated water and the remaining sulfides are therefore subjected to rapid oxidation. As a measure of the rate of oxidation it can be mentioned that one of the specimens analyzed is from a "stalactite" of copper sulfate, 2 dm in length, which was found in a tunnel only one year old.

The two values from Bisbee in column C, Figure 1, represent supergene sulfides. They are seen to differ only slightly from the "primary" sulfides, but the direction of change is in accordance with theoretical considerations. A certain increase in S^{32} in supergene sulfides might be expected if the sulfur of the sulfate in ground water (with the same $S^{32}:S^{34}$ ratio as the source

[1] The Falun values are also presented in Table 1.

sulfides) contributes to their isotopic composition. For if it really comes to an exchange reaction between these sulfates and sulfides and/or H_2S with isotope fractionation, the new sulfides must be enriched in S^{32} as compared with the sulfates. A pre-requisite for such a process would be that oxidation-reduction isotopic exchange could be realized below the zone of oxidation proper. However, the dissimilarities between primary and secondary sulfides in the material from Bisbee are too small to be taken as a definite indication of such a process.

Co-existing Sulfides and Sulfates of Hypogene Origin.—In several of the earlier publications on sulfur isotope fractionation it was shown that vein deposits containing both primary sulfides and sulfates are characterized by an enrichment of S^{34} in the sulfates as compared with the sulfides. In the primary sampling for the present investigation two samples were taken in order to examine this relationship between sulfide and sulfate, Durham, Figure 1, column IV and Table 5, and Falun, Figure 1, column III (the value under P, $\delta = +4.9$) and Table 1. The Durham sample was taken from the mineral collections of the Mineralogical Institute of Stockholm, and probably represents a barite vein with subordinate amounts of galena, belonging to a system of veins associated with basic intrusions in the Carboniferous sediments of northern England. In both cases an enrichment of S^{34} in the sulfate as compared with the sulfide is found to exist.

Sakai (14) pointed out that since the isotope fractionation is dependent on temperature the enrichment-factor in co-existing sulfide and sulfate could be taken as a geologic thermometer, provided that isotope equilibrium had been realized. It is always very difficult to make reliable statements as to a pre-existence of equilibrium conditions, but still the possibility of temperature estimation is worth consideration. For instance, it seems reasonable from a geological point of view that the Durham veins were formed at lower temperatures than the Falun ores and this may therefore account for the different enrichment-factors in the two cases.

Irrespective of the possibility of estimating the temperatures of formation, the sulfur isotope compositions in co-existing sulfide and sulfate clearly show that isotope fractionation between sulfide and sulfate phases does occur under hydrothermal conditions. Therefore, if in a certain sulfide ore district conditions for formation of sulfate ions may or may not be realized, such divergencies could also account for considerable variations in the isotope compositions of the sulfides of the district, provided the amount of sulfate sulfur was sufficient to cause a palpable concentration of the total number of S^{34} atoms in the sulfates. In order to ascertain whether such ideas can be supported by the distribution of S^{32} and S^{34} in co-existing sulfates and sulfides, sulfide samples were analyzed from various deposits, similar with respect to sulfide mineralization, but differing in content of sulfates.

The Skellefte District in northern Sweden is characterized by hydrothermal sulfide ore deposits of a type similar to the Boliden and Falun ores, which have been characterized with regard to their geological features in a previous paragraph [see also Gavelin (4)]. It was also stated that the sulfur isotope composition of various sulfides from the Boliden mine (Skellefte District)

shows only slight variations. The homogeneity of the sulfur isotope composition over wide areas in the entire district is quite remarkable. Thirty one analyses of sulfides from 11 deposits, covering a belt 100 km long and 20–50 km wide were found to vary between $\delta = +1.0$ and -3.5, 23 of these values varying between $\delta = -0.1$ and $\delta = -1.7$. If two additional values of a sulfide ore, somewhat different from the others, are also included the upper δ-value for the range of variation would be $+2.2$.

Barite has been observed in some of the ores from the Skellefte District but it is generally a rare constituent. In one case, however, namely that of the Åsen ores, barite forms an essential constituent. Thus, the average content of barite in one of the main ore bodies from Åsen was computed to be 8 percent.

At least four ore lenses occur in the Åsen ore within a mineralized zone 4 km in length. The mineral composition of the ores and the wall rocks does not display any particular features when compared with most of the other deposits in the Skellefte District, namely pyrite ore bodies with subordinate chalcopyrite and sphalerite in sericite-quartz schists. The isotopic composition of sulfur in several samples from drill holes has been determined, both sulfide sulfur and sulfate sulfur being analyzed. The results are presented in Table

TABLE 5

HYPOGENE SULFIDES AND SULFATES FROM THE SAME LOCALITY

Analysis no.	Mineral	Locality	Characteristics of specimen	δ
8	Barite	Durham, England	Massive barite with crystals of galena	+17.2
9	Galena	Durham, England	The same specimen as no. 8	−2.4
169	Barite	Åsen, Drill hole 8, 39.7 m	Massive barite	+10.7
250	Barite	Åsen, Drill hole 55	Massive barite with pyrite impregnation	+10.3
254	Barite	Åsen, Drill hole 58, 113,1–113,5 m	Pyrite ore with barite bands	+8.4
256	Barite	Åsen, Drill hole 12, 38.1–38.7 m	Massive barite with pyrite impregnation	−2.1
258	Barite	Åsen, Drill hole 1, 22.6–23.9 m	Massive barite with pyrite impregnation	+9.6
294	Barite	Åsen, Drill hole 6, 35.0–35.1 m	Pyrite-barite ore	+1.0
234	Pyrite	Åsen, Drill hole 55	The same specimen as no. 250	−0.5
255	Pyrite	Åsen, Drill hole 58, 113,5–113,5 m	The same specimen as no. 254	−5.6
257	Pyrite	Åsen, Drill hole 12, 38.1–38.7 m	The same specimen as no. 256	−14.8
259	Pyrite	Åsen, Drill hole 1, 22.6–23.9 m	The same specimen as no. 258	−1.7
293	Pyrite	Åsen, Drill hole 6, 35.0–35.1 m	The same specimen as no. 294	−10.5
260	Pyrite	Åsen, Drill hole 7, 34.1–35.5 m	Compact pyrite ore	−7.9
261	Pyrite	Åsen, Drill hole 9, 33.7–39.7 m	Compact pyrite ore	−7.1
262	Pyrite	Åsen, Drill hole 10, 31.9–33.1 m	Compact pyrite ore	−6.0
263	Pyrite	Åsen, Drill hole 6, 34.5–36.3 m	Pyrite-barite ore	−10.2
264	Pyrite	Åsen, Drill hole 15, 26.4–26.7 m	Compact pyrite ore	−6.7
265	Pyrite	Åsen, Drill hole 23, 32.8–35.5 m	Compact pyrite ore	−4.8
266	Pyrite	Åsen, Drill hole 24, 52.4–52.5 m	Pyrite impregnation in quartz-sericite-schist	+8.4
292	Pyrite	Åsen, Drill hole 24, 52.3–53.1 m	Pyrite impregnation in quartz-sericite-schist	+7.2
267	Pyrite	Åsen, Drill hole 25, 30.5–33.0 m	Compact pyrite ore	−6.0
268	Pyrite	Åsen, Drill hole 29, 44.6–45.3 m	Compact pyrite ore	−11.8

5 and in Figure 1, column IV. Two of the drill hole sequences are represented by two samples each; the analyses from the same section are united by unbroken lines. The two unbroken horizontal lines in column IV, Figure 1, denote the range of variation of the "typical" sulfide ores of the Skellefte District, the broken line indicates the upper limit of this range if two additional values representing the more special ore type mentioned above are also considered.

A conspicuous fractionation of the isotopes between sulfate sulfur and sulfide sulfur in most of the specimens is clearly indicated. In addition, two points of particular interest are: 1. The majority of the sulfide values are definitely enriched in the lighter isotope as compared with sulfides from the other ores of the Skellefte District; 2. The range of variation of sulfide sulfur is approximately five times wider in the Åsen ore field as compared with the total Skellefte District, if only the most typical ores are considered.

It seems logical to interpret the partial enrichment of the lighter isotope in the sulfide sulfur and the much wider range of variation of sulfur isotope composition in the Åsen ores, as compared with the other ores of similar type in the Skellefte District, as a result of local reduction-oxidation processes realized to an extent not possible in the other sulfide deposits of the district. The content of barite in the Åsen ores can naturally not be taken as a measure of the accurate proportions $SO_4 : H_2S$ in the ore-forming fluids, since it only gives an idea of the amount of sulfate actually precipitated. The content of barite may therefore equally as well suggest the amount of barium present during mineralization. On the other hand, the high percentage of barite definitely proves that sulfate ions were present during mineralization.

Since one of the most conspicuous features as regards both sulfide and sulfate values is the wide range of variation, it can be concluded that the isotope exchange reactions developed differently in various parts of the ore field. The positions of the individual samples being considered it was found that the varying sulfide isotope values are distributed irregularly within the ore field. No accumulation trend of particularly high or low values in certain parts of the field seems to occur. On the other hand, if co-existing sulfate and sulfide values are compared, certain significant relations are found.

In the survey of the Åsen values in column IV, Figure 1 certain values seem to be quite anomalous: Two sulfide values (both, however from the same drill hole sequence) fall in the sulfate range, and two sulfate values fall in the sulfide range (all these values were checked by several determinations). In several cases it was possible to obtain both barite and pyrite from one sample. The isotopic composition of sulfur from co-existing pyrite and barite is presented in Table 6. The arrangement of analyses in the table corresponds to their relative position in the field from east to west. In spite of the fact that the sulfide and sulfate values both cover a wide range of variation the enrichment factor is seen to be almost constant. This indicates that sulfide and sulfate were precipitated roughly contemporaneously and also that conditions, at least close to an isotope exchange equilibrium, prevailed

TABLE 6

CO-EXISTING SULFATES AND SULFIDES FROM ÅSEN

Position	Barite		Pyrite		Enrichment factor
	δ	S^{32}/S^{34}	δ	S^{32}/S^{34}	S^{32}/S^{34} pyrite + S^{32}/S^{34} barite
Drill hole 6	+1.0	22.203	−10.5	22.460	1.012
Drill hole 1	+9.6	22.014	−1.7	22.263	1.011
Drill hole 12	−2.1	22.272	−14.8	22.559	1.013
Drill hole 58	+8.4	22.040	−5.6	22.350	1.014
Drill hole 55	+10.3	21.998	−0.5	22.237	1.011

during precipitation. However, the precrystallization exchange reactions must have been governed by local unidirectional processes acting at intervals during the mineralization. For instance, it could be surmised that gaseous reducing or oxidizing agents might have caused a quantitive transformation of sulfate to hydrogen sulfide or vice versa.

In summing up, the results from the Åsen ore field clearly show that fractionation of the sulfur isotopes may be realized also at early stages of mineralization processes leading to a formation of sulfide ores of a comparitively high-temperature type, but also that such exchange reactions may be of local importance.

VARIATIONS OF ISOTOPIC COMPOSITION IN SULFUR FROM SULFIDES IN A HAND SPECIMEN

Jensen (7) pointed out that quite remarkable variations in the isotope composition in co-existing sulfides may exist. A similar observation was also made in the present investigation. Table 7 and Figure 1, column 5, present two examples of such variations. The specimen from Aachen represents a colloform zinc ore from Diepenlinchen ("Schalenblende" according to German nomenclature). The ore consists mainly of zincblende appearing as narrow layers of varying coloration—from light yellow to dark brown. One band of galena and several bands or nodules of pyrite also occur (Fig. 3). The specimen was chosen for a comparison with the colloform zinc ore from Cornwall which had anomalous light sulfur (no. 156) in order to see if such types of ore are generally characterized by particularly light sulfur.

As is seen from Figure 1, the sulfides of the colloform ore specimen from Aachen display remarkable variations in the isotopic composition but it is by no means characterized by particularly light sulfur. There is no general trend of variation from the inner to the outer parts in the zonal distribution of the sulfides. A significant difference between the various minerals is obvious, however: Pyrite is characterized by the heaviest sulfur, zincblende by intermediate values and galena by the lightest sulfur.

For comparison, galena and zincblende from a specimen from the same locality were also analyzed; they occur in a more coarse-grained form without colloform structure. These values are presented in the right part of column

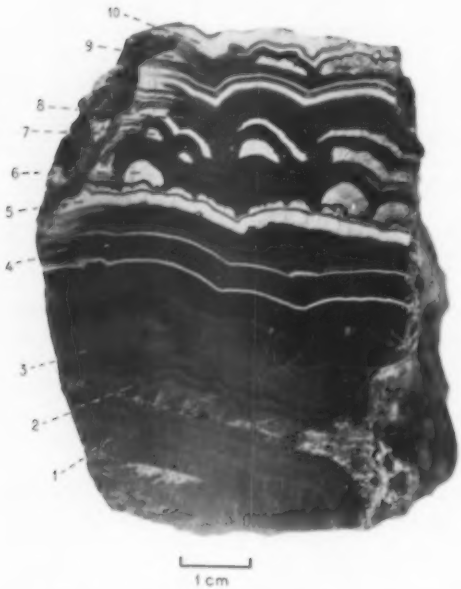

FIG. 3. Positions of samples analyzed from colloform ore specimen from Diepenlinchen, Aachen. The figures 1–10 represent the designation numbers of the samples given in Fig. 1, column V.

TABLE 7

SULFIDES WITH HIGHLY VARYING SULFUR ISOTOPE COMPOSITION IN THE SAME SPECIMEN

Analysis no.	Mineral	Locality	δ
180	Galena	Diepenlinchen, Aachen Figure 3	+2.6
182	Yellow sphalerite	Diepenlinchen, Aachen Figure 3	+12.6
203	Yellow sphalerite	Diepenlinchen, Aachen Figure 3	+18.8
208	Brown sphalerite	Diepenlinchen, Aachen Figure 3	+16.0
207	Brown sphalerite	Diepenlinchen, Aachen Figure 3	+11.5
181	Brown sphalerite	Diepenlinchen, Aachen Figure 3	+16.8
205	Brown sphalerite	Diepenlinchen, Aachen Figure 3	+13.0
183	Pyrite	Diepenlinchen, Aachen Figure 3	+24.1
206	Pyrite	Diepenlinchen, Aachen Figure 3	+25.7
204	Pyrite	Diepenlinchen, Aachen Figure 3	+26.5
184	Galena	Diepenlinchen, Aachen Medium grained zinc-lead ore without colloform structure	+8.3
185	Light-brown sphalerite	The same specimen as no. 184	+11.5
235	Pyrite. Kernel of concretionary nodule in Eocambrian sandstone	The Laisvall Mine	+29.9
236	Pyrite. Margin of the same nodule as in no. 235	The Laisvall Mine	+14.9

V in Figure 1. They fall within the range of variation found for the colloform sulfides. The analyses are too few to permit general conclusions but they could be taken to indicate that isotope fractionation developed more irregularly in the colloform ore types than in the more coarse-grained vein sulfides.

The other example of varying isotopic composition in sulfides from a single hand specimen refers to pyrite from the Laisvall mine in northern Sweden. The main ore is an impregnation of galena in late Precambrian sandstone forming an easterly border zone of the Caledonian mountain range (6). Pyrite occurs as disseminations in the sandstone, but it also forms concretionary nodules with radial structures. Since determinations of the sulfur isotope composition of some of these pyrite nodules by repeated analyses gave highly varying results a test was made where kernel and margin of one pyrite nodule were analyzed separately. A surprisingly high difference between the kernel ($\delta = +29.9$.) and margin ($\delta = +14.9$) was found. The diameter of the pyrite concretion examined was about 2 cm.

The two examples discussed above show clearly that fractionation of sulfur isotopes may develop quite differently even over very short distances during sulfide mineralization in nature. It is significant, however, that in both cases the material examined comes from typical low-temperature formations. It is very difficult to make a definite statement as to the cause of the divergencies in the examples given above. The Laisvall example is particularly peculiar since the diverging values are found in the same mineral species and nothing in the structural appearance of the pyrite nodule indicates different conditions of formation in various parts of the nodule. It is worth mentioning, however, that barite is a common constituent in the Laisvall ores, and that appreciable amounts of sulfate ions may therefore have been present during mineralization.

As regards the Aachen sample a certain correlation between kind of mineral species and sulfur isotope composition could be discerned. It can therefore be assumed that the same change of conditions for isotope fractionation also caused a change in the conditions of precipitation of sulfides. A sudden unidirectional reduction of sulfate would give an isotope composition of the sulfate type in the sulfides and perhaps such highly reducing agents are also apt to carry divalent iron in solution and may therefore account for a precipitation of iron sulfides (pyrite or marcasite) characterized by heavy sulfur. On the other hand, no correlation between iron content in sphalerite and the isotope compositions of the same sphalerites could be discerned in the material analyzed.

SUMMARY AND CONCLUSIONS

In summarizing the results of the present examination the following statements can be made. Agreement with earlier investigations on the same matters may sometimes make them generally applicable:

1. Sulfides representing various stages of a hypogene mineralization process generally do not differ significantly in their isotopic composition. In ore

districts characterized by a zonal arrangement of metals around certain emanative centers no simple correlation exists between spatial zonal arrangement of minerals and their sulfur isotope compositions. Therefore, if considerable variations of the S^{32}/S^{34}-ratios do exist within an ore body or in an ore district no general trend of variation can be stated from high-temperature to low-temperature formations. Nevertheless there commonly seems to be a tendency for the low-temperature sulfides to have a wider range of variation as compared with the high-temperature sulfides of the same mineralization.

2. Supergene oxidation of sulfide minerals is a unidirectional process involving no change of isotopic composition during the transformation of sulfide to sulfate. If conditions are such as to permit sulfate formed by oxidation of primary sulfides to contribute to the sulfur content of redeposited supergene sulfides below the zone of oxidation this process may cause an enrichment of light sulfur in the supergene sulfides, as compared with the primary minerals.

3. During hypogene sulfide mineralization a certain fractionation of the sulfur isotopes may occur. This is evidenced by significant divergencies in the S^{32}/S^{34}-ratios in co-existing sulfides and sulfates. The fractionation seems to have been more pronounced at low temperatures than at higher temperatures.

4. Isotope fractionation, particularly if developing under low temperatures, may be very local and vary appreciably over short distances.

On the basis of the above statements some general conclusions can be made on the use of determinations of sulfur isotope composition in discussions of ore genesis. It is obvious that oxidation-reduction processes may cause considerable isotope fractionation in hypogene sulfide mineralization even at fairly high temperatures. It is merely fortuitous if the presence of appreciable amounts of sulfate ions in the earlier stages of a mineralization process is evidenced by the occurrence of sulfate minerals in the mineral assemblage formed. Therefore it might be surmised that also in an ore district, where appreciable variations in isotope composition are established, the fractionation of sulfur with an originally homogenous isotope composition is the cause of these variations. For instance, the wide range of variation found in the sulfides of the Cornwall District might be due to a varying development of such oxidation-reduction processes. It is interesting to note in this connection that three out of the six samples characterized by the lightest sulfur in the Cornwall District, are from localities where barite was mentioned in the descriptions of the mineral assemblages. A closer examination of the mineral assemblages would perhaps reveal that conditions in the Cornwall Area are analogous to those of the Åsen ore field where the relations between isotopic composition in sulfide and sulfate respectively is obvious. It seems reasonable to assume that reduction-oxidation processes may be governed by certain properties inherent in the rock masses penetrated by the ore solutions. This would account for the agreement in isotope values sometimes found within restricted portions of an ore district, otherwise, characterized by a wide range of variation.

The above considerations disclose, that a few determinations of the isotopic composition of sulfur in sulfide minerals cannot give any definite information on the source of the sulfur—for instance if it is of a "sedimentary" or of a "magmatic" origin. If it is possible for isotope fractionation to occur at higher temperatures in connection with hypogene mineralization, variations in isotopic composition in an ore district offer then no definite evidence for a process involving mixtures of sulfur from various sources.

A significant number of determinations, however, may elucidate some precrystallization processes during mineralization. Some aspects of these matters will be considered in a later article dealing with Swedish sulfide occurrences of different geologic ages and environments.

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STOCKHOLMS HÖGSKOLA, STOCKHOLM VA,
RIKSMUSÉET, STOCKHOLM 50,
KAROLINSKA INSTITUTET, STOCKHOLM 45,
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A SULFUR MUD DEPOSIT FORMED THROUGH BACTERIAL TRANSFORMATION OF FUMAROLIC HYDROGEN SULFIDE

PONTUS LJUNGGREN

ABSTRACT

About 50 km to the south of Guatemala City there is a lake of volcanic origin, Ixpaco, diameter 300 m, the bottom of which consists of sulfurous mud, containing about 30 to 60% S. Fumarolic activity is still taking place along the shores of the lake, depositing orthorhombic sulfur crystals and pickeringite. The sulfur of the mud is amorphic μ-sulfur, grain size 0.01–0.1 mm, which, exposed to the air, changes into orthorhombic sulfur. The mud sulfur is formed through the action of sulfur bacteria, that transform H_2S of the fumaroles into sulfur and sulfuric acid, acidifying the lake water to pH 2.3. Total reserves of sulfur mud are estimated at several hundred thousand cubic meters.

INTRODUCTION

In the vicinity of the now extinct volcano Tecuamburro some 50 km to the south of Guatemala City, a widespread fumarolic activity has taken place. Some of these fumaroles have deposited considerable quantities of geyserite and native sulfur. There are several such deposits on the slopes of the volcano. The sulfur reserves of the deposits are estimated at a few hundred tons up to more than 20,000 tons.

On a plain about four km to the north of Tecuamburro there are several "playitas" or small beaches without vegetation, with outlets of H_2S and, in some places, hot springs. Considerable precipitation of sulfur is taking place in these hot springs.

A few hundred metres to the east of these "playitas" there is a small lake, "Laguna Ixpaco." The lake occupies the depression of an old crater at the bottom of a valley to the north of the volcano Tecuamburro (Fig. 1). The altitude of the lake is 1,120 m (4, p. 41).

The lake is circular with a diameter of 300 m. The water depth varies from one to two metres in the southern part, and from nine to twelve metres, or even more in some hollows, in the northern part. The color of the water is grayish yellow, due to a suspension of fine-grained sulfur particles. The bottom of the lake consists of sulfurous mud of clay consistence.

MINERALS DEPOSITED ON THE SHORE OF THE LAKE

Along the eastern shore of Lake Ixpaco there are several outlets of hot vapors. Around these fumarolic outlets deposition of various minerals takes place, mainly however of native sulfur. This fumarolic sulfur occurs as

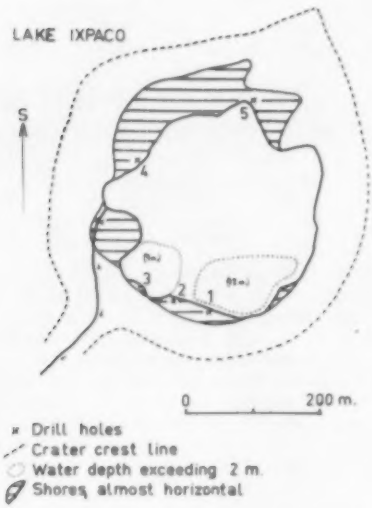

FIG. 1. Sketch map of Lake Ixpaco, 50 km to the south of Guatemala City, Central America.

orthorhombic crystals up to 10 mm in length. Those crystals formed from the hottest vapors are mainly developed as skeletal crystals.

Together with the sulfur crystals there is commonly a deposition of a white fibrous substance, which consists of pickeringite, $MgAl_2(SO_4)_4 \cdot 22H_2O$ (Fig. 2). The pickeringite of Ixpaco is also commonly in the form of a crust, up to 4 cm thick, deposited on the sand at the shore of the lake. Wet mud, when taken from the lake and placed upon the sand to dry, leaves a residual crust of pickeringite.

Mixed with the pickeringite, a few crystals of gypsum have been identified by microscopic examination.

THE WEATHERED GEYSERITE

On the northeastern shore of the lake there are some white cliffs (10 m to the north of locality 3, Fig. 1), the rock of which is more or less impregnated with sulfur. A microscopic examination reveals that these rocks consist of a highly weathered opaline material. The refractive index varies between 1.43 and 1.45. The specific gravity of the dry rock is 0.55. Differential thermal analysis and X-ray analysis show the presence of an opaline material together with a small quantity of α-tridymite.

It is evident that these rocks were formed originally by deposition of amorphous silica from hot springs (geysers). The presence of such weathered geyserites at some other sulfur deposits at the volcano Tecuamburro itself indicates a previous period of more intense thermal activity than at present.

Crystalline sulfur is found as vein fillings or replacements within the weathered geyserite. In some places the former geyserite has been almost completely replaced by sulfur; in other places there is a yellow coating of newly deposited sulfur upon the white geyserite.

The hot springs carried in solution a small percentage of copper, now found as thin crusts of copper carbonate and sulfate.

THE SULFUR MUD OF LAKE IXPACO

The sulfur mud, which makes up the bottom of the lake, consists of the following minerals: sulfur, quartz, pyroxene, titanomagnetite, opaline material, cristobalite, and clay minerals.

The sulfur is found as small drops or irregular grains, the grain-size being 0.01–0.1 mm, with a very few grains ranging up to one millimeter or even more (maximum observed, 5 mm). This sulfur occurs in the mud as μ-sulfur, which is an amorphic variety of sulfur not soluble in carbon disulfide. When exposed to the air it rapidly changes into the orthorhombic form (checked by X-ray analysis). The sulfur imparts to the mud a yellowish gray color.

Quartz occurs as irregular grains, mostly 0.01 mm in size or smaller. The pyroxenes belong to the enstatite type. They are elongated (mostly quotient length/breadth = 4/1) and, in most cases, intensely altered. A few remnants of augite have been observed. The grain-size of the pyroxenes varies between 0.05 and one millimeter. The titanomagnetites do not seem to be

FIG. 2. Hot water pool, 10 cm from the lake, with ascending hot vapors. Deposition of sulfur and pickeringite (white crusts) on the shore. The water of the lake is somewhat turbid, due to a suspension of fine-grained sulfur particles.

affected by the alterations. The grain-size varies between 0.05 and 0.5 mm. Some very small grains possess the optical characteristics of opal, having a refractive index of 1.46–1.48.

A considerable part of the mud is made up of clay minerals, many of which have the crystallographic outlines of preexisting minerals (probably plagioclases rich in anorthite). X-ray analysis of the mud gives the patterns of kaolinite, together with cristobalite and quartz. No clay mineral other than kaolinite has been found in the samples examined. Chemical analyses of the mud show the sulfur content to vary between 30 and 60 percent. The rest of the mud is mainly clay minerals and silica. A semi-quantitative spectrochemical analysis gave the following results, given as percentages (analyst: The Colorado Assaying Co.):

Silicon	major	Potassium	.1	Copper	.001–.01
Aluminium	5. –10.	Barium	.02	Gold	None
Iron	1. – 5.	Strontium	.01	Silver	none
Titanium	1.	Manganese	.01	Selenium	not detected
Sodium	1.	Vanadium	.001–.01	Sulfur	58.05 (qualitative test)
Calcium	1.	Chromium	.001–.01		
Magnesium	.2– 1.	Nickel	.001–.01		

A recalculation of this quantitative and semi-quantitative analysis, with due consideration to the optical and X-ray examinations, gives the following approximate mineral composition of the sulfurous mud:

Sulfur	58%
Kaolinite	22
Pyroxene	2
Titanomagnetite	1
Silica (quartz, cristobalite, opaline material)	17
	100

TEMPERATURES OF VAPORS AND WATERS

During the last fumarolic period of Ixpaco the most intense outlet of hot vapors took place along the northern side of the lake, resulting in the formation of the geyserite cliffs, mentioned above, and of thick layers of sulfur on the shore (between localities 2 and 3, Fig. 1). There is still intense fumarolic activity at this part of the lake. At locality 2 of Figure 1 hot vapors are ascending through the sand, depositing sulfur and pickeringite. Some small water pools with ascending hot vapors are also found at this place within a few decimeters from the shore line (Fig. 2). In the lake there is a hollow, 9 m deep, just outside localities 2 and 3, from the bottom of which there is an intense outlet of steam. About 30 years ago there was a constant water fountain in the middle of this hollow, which indicates that the fumarolic activity has been decreasing during the last years.

The temperatures of the waters and vapors of these different places have been measured (March 26, 1957) and the results are given below. The air temperature varied during the measurements between 25° and 28° C.

I. Hot vapors at the sulfur-incrusted parts of the shore:
87°, 94°, 95°, 96°, 95°, 94°, and 93° C.

II. Hot vapors ascending through the sand:
94°, 82°, 89°, 89°, 88°, 93°, 90°, and 80° C.

III. Water of small water pools with ascending hot vapors:
92°, 90°, 88°, and 87° C.

IV. Water of Lake Ixpaco, different places:
eastern shore 31° C, southern shore 32° C, western shore 32° C, and northern shore 29° C.

V. Water of the outlet of the lake: 32° C.

VI. Waters of small brooks entering the lake:
24°, 21°, 20°, 20°, and 26° C.

CHEMISTRY OF WATERS AND VAPORS

The water of the lake has a grayish yellow color, due to the suspension of small particles of sulfur. The surface of the water has a thin cover of such particles which through the action of waves and winds are carried to the shores of the lake, resulting in deposition of sulfur-rich sands.

Some chemical analyses gave the following results, given as grams per liter:

	SO_4	H_2S	Cl
Pool of hot water (92° C) at the sand shore with intense gas outlet	.46	.10	.02
Water from the deep part of the lake, at a site of intense gas emission	1.17	.18	tr.
Water from the outlet of the lake	1.30	nil	nil

Only a small part of the water of the hot water pool is condensed water from ascending vapors; the largest part is water infiltrated from the lake through the sand. This means that the content of sulfate ions of the hot water pool, as indicated above, is not representative of the water condensed from the vapors or delivered as hot water from deeper levels. It is possible, as will be shown below, that these originally fumarolic waters have but a negligible percentage of sulfate ions. The figures given above indicate that hydrogen sulfide is predominant at the sites of gas outlets whereas sulfate ions are predominant in the main parts of the lake. Qualitative tests have been carried out within different parts of the lake, confirming the data given above: sulfide ions are almost absent within the parts of the lake where no gas outlet occurs; sulfate ions are less common at places of intense gas outlet than within the other parts of the lake.

An interesting qualitative test was carried out of condensed water from the ascending vapors at the sulfur-incrustated part of the shore (vapor temperature 95° C). This water had a very high percentage of sulfide ion but sulfate ions were not detected. A silver coin was instantly blackened when kept in the hot vapors. The smell of hydrogen sulfide is very strong at all places of gas outlet. Tests for SO_2 or SO_3 in these vapors were negative.

ACIDITY OF DIFFERENT WATERS

The pH of the different waters has been measured, with the following results:

I. Pool of hot water (92° C) at the sand shore with intense gas outlet (Fig. 2)	pH 2.92
II. Water from the lake	pH 2.27
III. Water from the outlet of the lake	pH 2.40
IV. Condensed fumarolic water from the sulfur-crusts of the shore	pH 5.0

An approximate measurement of the pH of a small brook that enters into the lake on its southern side gave pH 7. The figures given above provide evidence of the fact that the high acidity of the lake water is primarily not due to the fumarolic vapors and waters, as these have a comparatively high pH (about 5), but rather to reactions taking place in the water of the lake. The fumarolic vapors consist mainly of water, carbon dioxide, and hydrogen sulfide, the percentages of which are sufficient to acidify the condensed water to a pH of about 5.

THE SULFUR BACTERIA

A microscopic examination of the uppermost parts of the sulfurous mud of Lake Ixpaco reveals the abundance of sulfur bacteria, belonging to the Family *Beggiatoa* (5, pp. 197, 294–295). These bacteria transform hydrogen sulfide into free sulfur and sulfuric acid (1, p. 73), thus:

$$2\,H_2S + O_2 \rightarrow 2\,H_2O + 2\,S \quad \text{and} \quad 2\,S + 3\,O_2 + 2\,H_2O \rightarrow 2\,H_2SO_4.$$

The bacteria of this family store small globules of elemental sulfur within the cells, and, during periods of H_2S shortage, this sulfur is consumed to form sulfuric acid. It is probable, that most of the elemental sulfur (amorphic small grains of sulfur, insoluble in carbon disulfide, μ-sulfur) of the mud is formed through the action of these sulfur bacteria, and it is also probable that the high acidity and the sulfate ion content of the lake water is due, as mentioned above, to the bacterio-chemical reaction during which sulfuric acid is formed.

The sulfurous mud of the lake consists of sulfur-rich layers alternating with layers rich in decomposed volcanic ash, and also, near the shore lines, of layers rich in sand washed from the surrounding slopes during the rainy seasons. The local ashes and sands consist mainly of feldspars (anorthite-rich plagioclases) and pyroxenes, together with some olivine, titanomagnetite, and quartz (3). The silicate minerals are rapidly decomposed by the sulfuric acid delivered by the sulfur bacteria, and this is the reason why no feldspars or olivine and only few pyroxenes can be seen by microscopic examination of the mud. These silicate minerals have been transformed into clay minerals through the action of the sulfuric acid (2, p. 297). This is also the reason for the common occurrence of pickeringite, an aluminium magnesium sulfate that is formed during this process from the silicates of the mud.

The grain-size of the sulfur globules within the bacteria is the same as that of the sulfur of the mud, 0.01 mm or a little more.

An approximate calculation gave about 100,000 sulfur bacteria per cubic centimeter of the mud. These bacteria are also very abundant in the lake water.

The outflow of water from the lake, during the dry season, is estimated to about 10 litres per second, at least half of which has arrived at the lake as small brooks or as ground water from the slopes surrounding the lake.

THE SULPHUR SAND

In some places along the northern and eastern shores there is a sand consisting almost entirely of grains of sulfur, the grain-sizes being 1–5 mm. This sulfur is, in contrast to the sulfur of the mud, immediately soluble in carbon disulfide. X-ray examinations show the sulfur to be orthorhombic. The sulfur grains are shaped as lenses, the smallest grains are convexo-plane, the larger ones are convexo-concave. It is probable that this sulfur is formed inorganically, contrary to the sulfur of the mud, which is formed through the action of sulfur bacteria. The proximity of the fumarolic outlets provides a possible explanation of the origin of this sulfur, namely as directly sublimated in the water and floated to the surface of the lake, by means of gas bubbles, which existed at the now concave part of the grains. In this sand there are no spherical grains of sulfur, indicating that no remelting has taken place. At one place on the sand shore a layer made up entirely of such sulfur grain lenses was found, the thickness being three decimeters (drill hole No. 2).

CORE DRILLINGS AT THE SHORE OF THE LAKE

Four drillings were carried out at different sites around the lake, as indicated on Figure 1.

Drill hole No. 1:

0.0–0.5 m	sand
0.5–2.3 m	sand and sulfur-rich clay (< 30% S)
2.3–4.5 m	sulfurous mud (> 30% S)
4.5–4.7 m	black sludge

Drill hole No. 2:

0.0–0.2 m	sand
0.2–1.0 m	sulfur sand (with sulfur lenses)
1.0–2.0 m	sulfur-rich clay (20–40% S)

Drill hole No. 4:

0.0–0.3 m	black sludge (above water level of the lake)
0.3–0.5 m	sulfur-rich sand (< 30% S)
0.5–1.5 m	sulfur-rich clay (20–40% S)
1.5–2.0 m	black sludge

Drill hole No. 5:

0.0–0.5 m	sand and black sludge
0.5–1.0 m	sulfur rich sand (< 30% S)
1.0–4.8 m	sulfurous mud (> 30% S)
4.8–5.0 m	sulfur-rich sand (< 30% S)

SULFUR RESERVES

The sulfur reserves of Lake Ixpaco (sulfurous mud) are estimated at considerably more than 100,000 cubic meters.

Department of Mineralogy and Geology,
University of Lund, Sweden,
July 1, 1959

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GEOLOGY, SULFUR ISOTOPES AND THE ORIGIN OF THE HEATH STEELE ORE DEPOSITS, NEWCASTLE, N. B., CANADA

E. DECHOW

ABSTRACT

The Heath Steele mine is located 35 miles northwest of Newcastle, New Brunswick, Canada.

Middle Ordovician Tetagouche Group rocks, consisting of siliceous and basic volcanic rocks and fine-grained quartz sericite schists and porphyry, have been folded into a steeply plunging recumbent anticline. The ore deposits of zinc, lead, and copper are associated with minor folding and or sheared dilatent zones at or near the contact between porphyry and fine-grained sericitic schist.

Mineralogically the sulfide bodies consist of early, euhedral arsenopyrite, magnetite, and pyrite, followed by interstitial pyrrhotite, sphalerite, chalcopyrite and galena. Minor minerals are tennantite-tetrahedrite, bismuthinite, marcasite, hematite, and some graphite. Supergene minerals consist of chalcocite, covellite and marcasite with a little native silver. Little hypogene replacement has taken place between the minerals, which show a "porphyritic" texture.

Sulfur isotope ratios have been determined for over 150 sulfide and sulfate specimens from five of the seven ore bodies, and from granite, acid and basic volcanics, porphyry, and sediments. The results indicate that there is no detectable fractionation either during hypogene mineralization or supergene enrichment. The spread (21.82–22.02) covered by the ratios is narrow, and suggestive of a well homogenized source of mineral solutions. The enrichment of S^{34} in the ore sulfides and the presence of graphite, evident from mineralographic studies and mass spectrometric analysis, suggests reduction of original sulfates (known to be enriched in S^{34}) by organic carbon at temperatures in excess of 600° C. A calculation based on the isotopic exchange reaction between sulfide and sulfate under equilibrium conditions and the spread of the ratios indicates a temperature of 700–800° C for the source. Finally the ratios determined for sulfides in a gneissic granite close to Heath Steele have the same ratio as the ore. These factors are considered to be diagnostic of a magmatic hydrothermal origin for the ore deposits.

In conclusion the writer believes that an original source bed has been buried until suitable temperatures were reached to cause granitization, reduction of sulfates, and mobilization of the resulting sulfides to form ore deposits at favorable loci.

INTRODUCTION

THE Heath Steele mine is located about 35 miles northwest of Newcastle, New Brunswick, Canada. Access is by means of a paved road from Newcastle or by Canadian National Railroad spur from Bartibog on the main Newcastle-Bathurst line.

The present study is a portion of a dissertation presented at Yale University in partial fulfillment for a Ph.D. degree. Field work was done during the summers of 1957 and 1958. Difficulties of mapping are typical of this part of New Brunswick and comprise intense dynamic metamorphism, lack of key beds, and a masking layer of glacial drift.

ACKNOWLEDGMENTS

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GENERAL GEOLOGY

The rocks underlying the Heath Steele property are Middle Ordovician in age and have been assigned to the Tetagouche Group. They consist of siliceous and basic volcanic rocks, fine-grained quartz-sericite schist, and varieties of porphyry (Fig. 1).

The quartz-sericite schists are dark gray, thinly laminated fine-grained rocks that occur interbedded with porphyry through the mapped area.

The composition of these rocks varies considerably. Generally they consist of bands of fine siliceous material 1–4 mm thick separated by thin bands of sericitic and chloritic material. The latter is considered to have been formed from original argillaceous or felspathic layers by low-grade metamorphism, and is therefore parallel to the original bedding. Following Pettijohn's classification the rocks originally had the composition of graywacke. Unfortunately their fine-grained nature prevented an accurate estimation of the amount of felspar present. Although they are referred to as sediments, their true origin is not certain, either they were true sediments or fine, waterlaid tuffs; in fact, rocks similar to the overlying siliceous volcanic rocks occur intercalated with them. Shaw (17) has described similar rocks to the south in the Sevogle River region. Smith and Skinner (19) have correlated the Heath Steele "sediments" with Shaw's formation, although Skinner (18) previously correlated them with the Upper Tetagouche argillaceous sediments. The writer considers them correctly correlated with the lower formation as they are unconformably overlain by the siliceous volcanic rocks.

Porphyry consists predominantly of quartz-felspar porphyry with minor quartz porphyry. The quartz-felspar porphyry consists of subhedral to euhedral quartz and felspar grains set in a matrix of quartz, felspar, sericite and chlorite. The felspars are generally embayed, brecciated and aligned sub-parallel to foliation, somewhat replaced by sericite and in places epidote and carbonate. Wisps, stringers and masses of sericite and chlorite trend

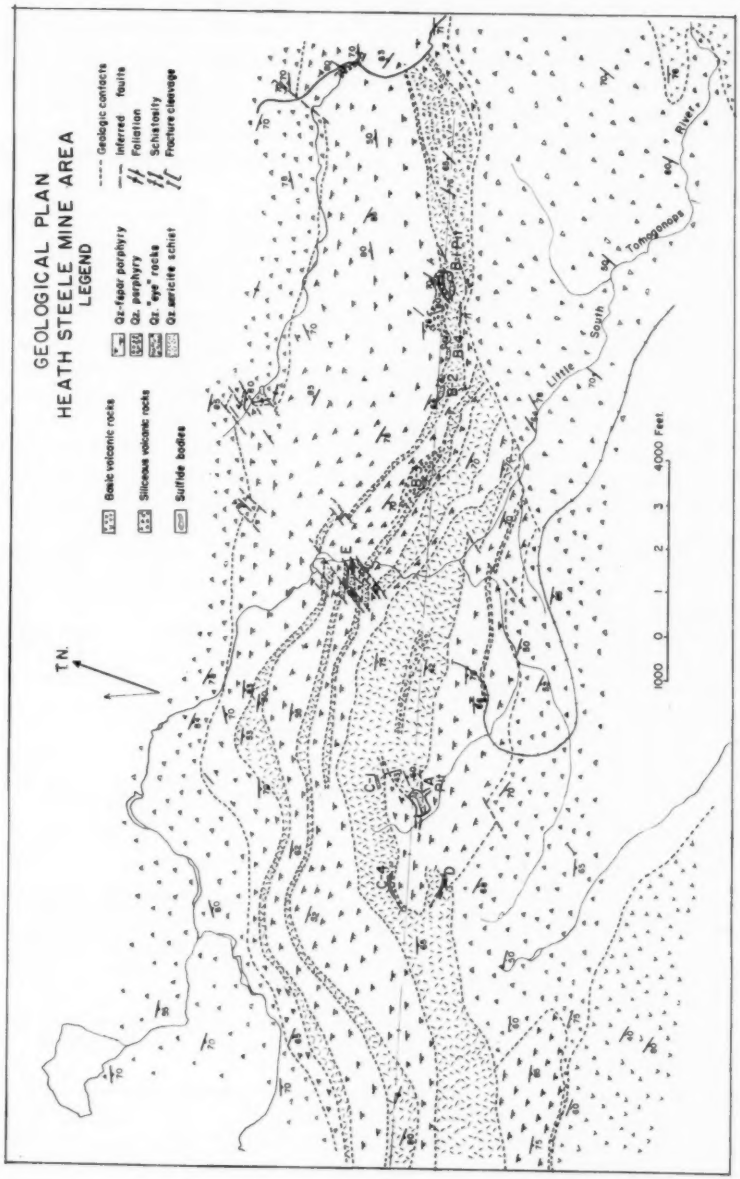

GEOLOGICAL PLAN
HEATH STEELE MINE AREA
LEGEND
Basic volcanic rocks
Siliceous volcanic rocks
Sulfide bodies
Qz-feldspar porphyry
Qz. porphyry
Qz. "eye" rocks
Qz sericite schist
Geologic contacts
Inferred faults
Foliation
Schistosity
Fracture cleavage
T.N.
Little South Tomogonops River
4000 Feet

FIG. 1.

across the fine ground mass and curve around the phenocrysts, giving the rock its schistose appearance. The origin of this porphyry is considered to be that of a group of intrusive sills, which may have been extrusive in places. In any case, they can be mapped locally as a conformable unit. Gourley (6) in a recent study considered these rocks to be coarse arkosic sediments. Whatever their origin they are important economically because the ore deposits are located along structural features in close proximitey to the porphyry-sericitic schist contact.

Quartz porphyry occurs only in large bodies north of the B-1, B-3 and B-4 bodies, but is abundant as thin bands in the E, A-C-D, and B-2 areas. It is intimately associated with the quartz-felspar porphyry and is considered to be a phase of it. The quartz phenocrysts are up to 3 mm in diameter, subhedral but sporadically euhedral, and set in a predominantly sericitic groundmass containing some penninite chlorite and muscovite.

Two lenses of a rock that resemble the quartz porphyry closely, have been labelled as "quartz eye" rocks. The eastern lens south of the B-1 pit appears to intertongue with the quartz-felspar porphyry and appears to be a phase of it. However, the quartz grains are smaller and angular. The other lens occurs within a thick sediment, band, is variable in composition and contains rounded phenocrysts so that it is correlated with the sediments rather than the porphyry.

South of the B zone the porphyry and sediment bands are cut off by the siliceous volcanic rocks. This has been interpreted as a minor unconformity, the formation of which is illustrated in Figure 2.

The siliceous volcanic rocks are composed predominently of a dark gray,

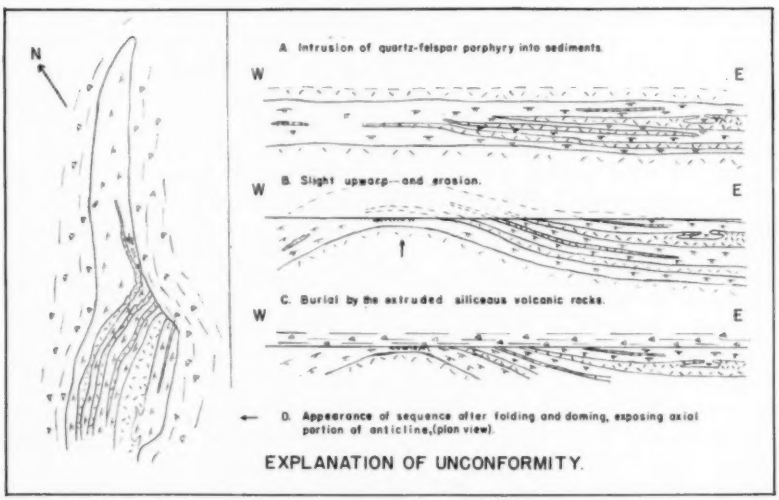


FIG. 2. Explanation of unconformity and structural history.

white weathering, schistose to banded rock containing scattered fine corroded and fractured felspar phenocrysts with or without minor quartz phenocrysts. The felspars are twinned plagioclases with a composition of andesine-oligoclase, or rarely untwinned albite. These have been commonly replaced by chlorite, sericite, epidote and carbonate, and are set in a fine-grained matrix of quartz, felspar, sericite and chlorite. The rock is considered to be tuffaceous for the following reasons.

1. The inclusion of fragments of chilled volcanic rock and interbedded agglomerates suggests a pyroclastic origin.
2. No primary flow structures, pillows or amygdules have been observed.
3. The rock is finely banded.

Basic volcanic rocks occur in the southeast and southwest portion of the mapped area. They are grayish green, massive, aphanitic in appearance and are composed predominently of secondary ferro-magnesian minerals forming a matrix for sausseritized felspar laths. The southeast body cuts across the general foliation, but the southwest body extends through the siliceous volcanic rocks almost to the contact with the porphyry. For these reasons the basic rocks may be intrusive, contrary to general opinion.

Although not occurring in the mapped area, the granitic rocks of New Brunswick should be mentioned for two reasons:

1. They appear to have played some part during ore genesis.
2. Because of their relation to the regional structure.

The granitic rocks are considered to be of pre-upper Devonian age (5). There are two varieties; a gneissic type considered to have been emplaced during deformation, and a massive type intruded after deformation. A body of the former type, 1 mile by 4 miles in size, with its long axis oriented north-northwest, occurs about three miles southwest of the D body, at South Little River Lake. This rock is composed predominantly of quartz and felspar with minor interstitial ferromagnesian minerals. The quartz occurs as discrete grains or in micrographic texture. The felspar is predominantly perthite with minor amounts of albite, oligoclase, and microcline. Sausseritization of the felspars is common and the ferromagnesian minerals have been altered to chlorite and minor amounts of amphibole. Pyrite is generally associated with the chlorite. Accessory minerals are iron oxides, apatite, fluorite, and zircon. The foliation, sporadically absent, in general strikes north-northwest parallel to a major structural flexure in this region.

The intrusive granites are gray, biotitic, medium to coarse-grained types that cut across all previous structures.

STRUCTURE

The regional structure of the Ordovician rocks of New Brunswick is separated into two units by a line trending north-northwest from North Little River Lake some two miles west of Heath Steele. Northeast of this line the dominant structures are two anticlinoria separated by a synclinorium. These are complex folds with steep plunges to the northeast. Along the major

structural axis extending north-northwest from North Little River Lake, a north-northwest cleavage is developed which is later than the north-northeast trending structures. In addition, the north-northeast striking rocks are deflected towards the southeast to the southwest of Heath Steele and faults parallel this trend to the west.

The geology in the Heath Steele area shows features that can be attributed to both these trends. A north-northeast foliation is developed in all the rocks. This is parallel to original bedding in the fine-grained rocks where it is caused by alternating bands of siliceous and sericitic material. It is emphasized in the porphyry by sub-parallelism of the feldspar laths. In general this foliation dips at 60° to 80° south, except near the B-1 and B-4 areas and in the northeast corner of the mapped area. In places where deformation was more intense this foliation grades into a schistosity, as in the fine-grained tuffs southwest of the D body and close to the ore bodies themselves.

The north-northwest trending structure is present over the mapped area as a fracture cleavage or jointing that displaces the north-northeast foliation. The porphyry and interbedded fine-grained bands north of the C-1 and C-4 bodies are folded along north-northwest trending axes.

The major structure of the mapped area has been interpreted as the axial portion of a steeply plunging recumbent anticline. The development of this structure is shown in Figure 2. Evidence for this, given in the writer's dissertation on Heath Steele, is; movement of dragfolding, dip and strike of foliation, similarity of volcanic rocks to north and south and agreement with regional structure.

Faulting and shearing is considered to trend in two main directions. An earlier east-west set that is closely associated with ore formation and a later north-northeast set that displaces the ore. This faulting is small scale in extent, being present in the porphyry but soon lost in the fine-grained rocks.

ORE DEPOSITS

General Description.—The Heath Steele ore deposits may be divided conveniently into three groups:

(a) *The B zones* comprise three ore bodies, B-1, B-4 and B-2, which occur along the flanks and noses of steeply plunging folds. They are associated with much iron formation and rake steeply towards the west.

(b) *The E zone* consists of four tabular sulfide bodies occurring in chloritic schist sandwiched between porphyry masses. They strike east-west and dip south at 50° to 60°. The central two bodies, which are the largest, coalesce at depth to form a high-grade copper lens that plunges steeply westward.

(c) *The A-C-D zones* are associated with an outlier of porphyry forming a basin-like structure in the sediments. The C and D ore bodies are located in zones of shearing close to the porphyry-sediment contact and the A body in undulations formed by this contact but cut by east-west faults.

All ore bodies are of the massive replacement type characteristic of the

Ordovician province of New Brunswick. They consist of massive pyrite that carries economic grades of base-metal sulfides in places. High-grade lead and zinc sulfides occur generally in the noses of folds as galena, sphalerite, and a little chalcopyrite. This is true of the A and B ore bodies. Chalcopyrite, pyrrhotite, and quartz occur where later fracturing has occurred within the massive pyrite, or where ore control was due predominantly to shearing as in the D ore body.

A mineralographic study showed the ore to consist of early, euhedral, arsenopyrite, magnetite and pyrite, containing interstitial pyrrhotite, sphalerite, chalcopyrite, and galena. Minor minerals are marcasite, bismuthinite, hematite, tetrahedrite-tennanite and some graphite. Supergene chalcocite, covellite, and marcasite exist in the near surface portions. Gangue minerals are quartz, chlorite, and carbonate.

No extensive hypogene replacement exists, instead the ore textures may be interpreted as "porphyritic" (Fig. 3), pyrrhotite and chalcopyrite fill later fractures and the sphalerite and galena with some chalcopyrite have migrated to areas of greater dilatency during crystallization. Marcasite occurs as a later hypogene alteration product of pyrrhotite. Supergene replacement as examined in B-1 pit is extremely fine-grained. Orthorhombic chalcocite occurs in minute fractures in sphalerite and chalcopyrite, completely replaces galena, but only forms a thin coating around pyrite. Covellite is later than chalcocite and generally replaces it (Fig. 4).

SULFUR ISOTOPIC STUDY

Methods and Apparatus

Drill core samples of pyrite, pyrrhotite, chalcopyrite and sphalerite-galena were collected from the B-1, B-2, E, A, and D bodies. To facilitate separation of the various minerals in this fine-grained ore, coarse-grained samples were preferred. Even so, sphalerite and galena could not be separated and were analyzed together. The samples of country rock containing sulfide were collected during mapping. Sulfate samples were of secondary sulfate formed on ore stock-piles at the surface or from mine waters in the pits. Sulfides were burnt directly to sulfur dioxide in a stream of oxygen at temperatures slowly raised to 1000° C, and this gas was dried by passage through a dry ice-acetone mixture before being analyzed on the mass spectrometer. Sulfate samples precipitated as barium sulfate were reduced with graphite at temperatures of 1000–1050° C to barium sulfide, to which was added hydrochloric acid and zinc dust and the resulting hydrogen sulfide precipitated as silver sulfide by bubbling through silver nitrate. The silver sulfide was then ready for combustion to sulfur dioxide and mass spectrometric analysis.

The mass spectrometric analysis has been described by Jensen (9). S^{32}/S^{34} ratios are reported as ratio values although in all tabulations the permil values are also given. In addition, a standard sample ($S^{32}/S^{34} = 22.21$) was periodically analyzed to check the accuracy of all results. This is given as Standard No. 2.

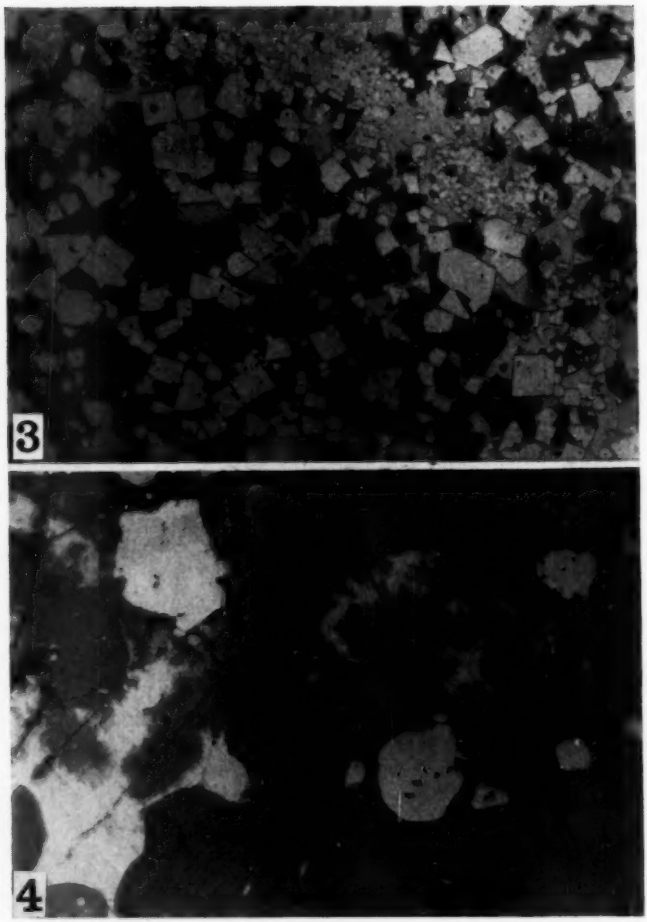


FIG. 3. High-grade lead-zinc ore showing "porphyritic" texture. Euhedral pyrite cubes, with blebs of sphalerite (gray), have massive sphalerite and galena (dull white) interstitial. Black mineral, showing some crystalographic outline is carbonate, etched with 1:1 HCl. × 41.5.

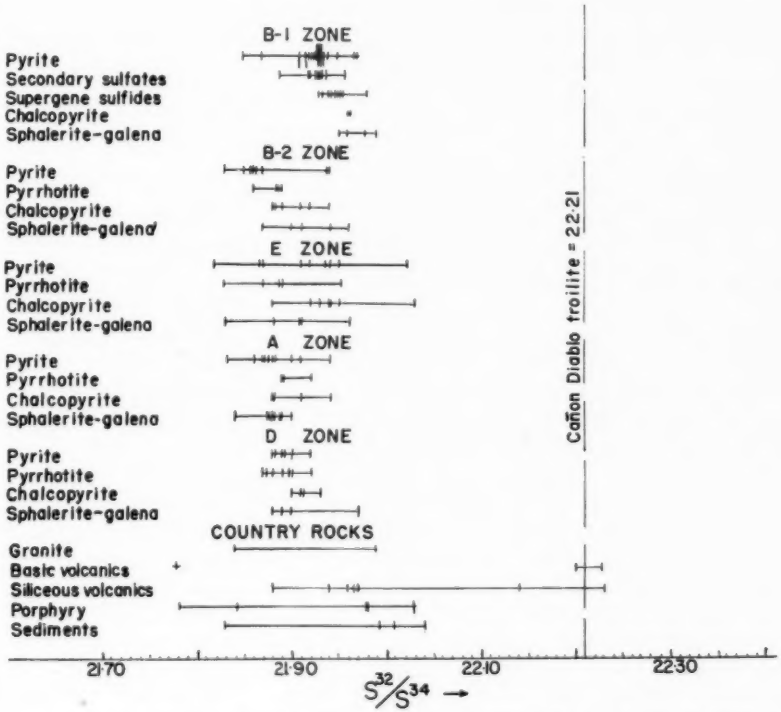
FIG. 4. Galena (dull white) mostly replaced by chalcocite (light gray), in turn replaced by covellite (dark gray). Sphalerite (gray) contains chalcocite along fine fractures. Pyrite grains (white, high relief) surrounded by a rim of chalcocite. × 160.

Discussion of Results

All results are plotted in Figure 5 and given with a description of the sample in Tables I–VII.

Role of Isotopes During Supergene Enrichment.—Supergene enrichment takes place in two stages. The first is the oxidation of sulfides to sulfates and the solution of soluble sulfates. The second stage is the replacement and enrichment of the primary ore where Eh and pH conditions are favorable.

The process of oxidation is quantitative and complete. All the sulfides present are converted to sulfate and therefore the sulfur in these sulfates will have the same isotopic composition as the original sulfides. This is shown in Table I and Figure 5. The enrichment process, however, is different, here there must be some exchange of sulfur atoms and therefore a mechanism by which isotopic fractionation might occur. As stated above, chalcocite is replaced by covellite but not vice-versa. According to Garrels (7), and Garrels and Naeser (8), at the pH and Eh for this to occur, the stable sulfur



SULFUR ISOTOPIC RATIOS IN ORE ZONES & COUNTRY ROCKS.

FIG. 5.

TABLE I

SULFATES

No. of sample	Description	Yield %	S^{32}/S^{34}	δ^{34} o/oo
A I	White sulfate collected from stockpile of Pb-Zn ore near Mill	77.4	21.92	13.5
B II	White efflorescence found on Pb-Zn concentrate after dry period.	84.2	21.94	12.2
C II	Secondary sulfate found on ore in stockpile from B-I ore.	83.4	21.94	12.2
D I	As above	66.4	21.98	10.4
D III	As above	89.2	21.93	12.60
D.H. 191–81 ft.	Sec. sulfate formed on core	—	21.93	12.60
E	Copper sulfate collected on twigs below B-1 pit where water had evaporated.	78.5	21.96	11.3
F II	Sulfate collected from edge of B-1 pit where water had evaporated.	86.4	21.93	12.60
G	Water sample from A pit, collected after dry period, 24 July 1958.	76.0	21.96	11.3
H	As above, collected 25 July 1958.	83.6	21.93	12.60
J	As above, collected 20 September 1958.	76.4	21.99	9.90
K I	Water from small pool below B-1 pit stockpile where concentrated by evaporation.	87.0	21.92	13.1
M	Water sample from B-1 pit collected 24 July 1958.	87.2	21.92	13.1
N	As above, collected 25 July 1958.	86.0	21.93	12.60
P I	As above, collected 20 September 1958.	85.8	21.93	12.6
Q	Water sample from B-1 pit sump, collected during operations in September 1957.	—	21.89	14.4

Standard No. 2 analyzed 22.22 ($\delta S^{34} = 0.0$) under the same conditions. A significant factor is that during reduction some fractionation occurred. Thus all samples from which the yield was greater than 80 percent varied from 21.92 to 21.94, while those which had a yield between 75 and 80 percent were enriched in the lighter isotope. However, for the B-1 samples the variation was 21.92 to 21.96, and the mean was 21.93 $\pm$ 0.01. This is identical to the ratios obtained for the primary sulfides (Table II). Sample Q is ignored as it was not reduced quantitatively and was precipitated as PbS, which undergoes a complicated dissociation (15).

species is H_2S. However, any sulfate already in solution under these conditions will not be reduced but will exist metastably (8, p. 129). This means that during enrichment any sulfur taking part will do so as H_2S, formed from primary sulfide in situ, and this will have an opportunity to undergo an isotopic exchange reaction with sulfate:

$$S^{32}O_4'' + H_2S^{34} \rightleftharpoons S^{34}O_4'' + H_2S^{32}.$$

At 25° C and one atmosphere pressure, this reaction is displaced towards the right hand side so that any additional sulfur atoms added during enrichment should be more highly concentrated in S^{32}. Figure 5 indicates that the supergene sulfides are slightly lighter than the sulfates but are still well within the total spread of ore ratios. Therefore it can be said that no detectable fractionation was observed during supergene enrichment. An explanation for this is the lack of opportunity for the above isotopic exchange reaction to attain equilibrium, i.e., nothing approaching a closed system.

Fractionation During Mineralization.—No positive fractionation during hypogene mineralization was detected. All mineral species cover the same

TABLE II

B-1 ZONE ISOTOPIC RATIOS

Sample No.	Pyrite		Sec. Sulfide		Chalcopyrite		Sphalerite-galena		DESCRIPTION
	S^{32}/S^{34}	$34_{/00}$	S^{32}/S^{34}	$34_{/00}$	S^{32}/S^{34}	$34_{/00}$	S^{32}/S^{34}	$34_{/00}$	
B-1 120			21.95	11.7					Fine sooty chalcocite completely replacing pyrite.
B-1 27	21.92	13.1	21.95	11.7					Fine pyrite replaced along vein by supergene sulfide.
30	21.92	13.1	21.94	12.2					As above.
69	21.92	13.1	21.93	12.6					As above.
24			21.94	12.2					Sec. sulfide replacing pyrite but cont. much pyrite.
116			21.95	11.7					As above
74			21.95	11.7					Cc. intimately mixed with pyrite.
80			21.98	10.4					Chalcocite replacing pyrite.
23	21.93	12.6	21.93	12.6					As above
4							21.96	11.3	Sphalerite and galena with sec. sulfide and pyrite.
5							21.98	10.4	As above.
106							21.95	11.7	Sphalerite in high grade Zn-Pb ore
62					21.96	11.3			Chalcopyrite in qz. veinlet cutting massive pyrite.
108					21.96	11.3			As above.
14					21.99	9.9			Sphalerite and galena cont. much pyrite.
11	21.92	13.1							Massive pyrite.
42	21.91	13.5							" "
41	21.93	12.6							" "
419-202	21.87	15.3							" "
-355	21.95	11.7							" "
421-208	21.97	10.8							" "
370-205	21.85	16.2							" "
-227	21.94	12.2							" "
327-230	21.93	12.6							" "
327-230	21.93	12.6							" "
373-395	21.97	10.8							" "
420-268	21.92	13.1							" "
418-169	21.91	13.5							" "
-200	21.93	12.6							" "
415-180	21.93	12.6							Massive pyrite
329A-182	21.93	12.6							" "
-185	21.93	12.6							" "
Mean	21.92 ±.02	13.1 ±.8	21.95 ±.01	11.7 ±.4	21.96 ±.00	11.1 ±0.0	21.97 ±.02	10.8 ±.8	

isotopic range. However, pyrrhotite may be enriched in S^{34} and chalcopyrite depleted. Thus 16 out of 19 pyrrhotite samples had values between 21.82 and 21.91 and 17 out of 21 chalcopyrites had values lying between 21.90 and 22.02 (Fig. 5). The total spread covered by the combined ratios is 21.82–22.02 which is exactly the spread of the pyrite values. It seems possible that during the crystallization of the intimately associated chalcopyrite and pyrrhotite the heavier isotope was absorbed into the pyrrhotite lattice. This trend is nevertheless not considered statistically significant.

Sulfides in Country Rocks.—Sulfide samples were collected from granite, basic, and siliceous volcanic rocks, porphyry and sediments, (quartz sericite schist). The granite samples were found in the South Little River pink gneissic granite. Both samples analyzed fell within the spread of the ore sulfides. The same can be said for the majority of samples analyzed. This is to be expected as they were all collected close to the ore bodies and therefore associated with ore formation. However, there are six exceptions to this. Two of these analyses, one in porphyry close to the B-2 ore body, the other in a basic volcanic rock south of the D zone where considerable deformation is present, have ratios of 21.78. Both may be associated with ore deposition in some way. Of the other four ratios, two occur in basic volcanic rocks

TABLE III

B-2 ZONE SULFUR ISOTOPIC RATIOS

Sample No.	Pyrite		Pyrrhotite		Chalcopyrite		Sphalerite-galena		Description
	S^{32}/S^{34}	δ^{34}o/oo	S^{32}/S^{34}	δ^{34}o/oo	S^{32}/S^{34}	δ^{34}o/oo	S^{32}/S^{34}	δ^{34}o/oo	
429-283	21.86	15.8	21.89	14.4	21.91	13.5	21.91	13.5	Coarse grained pyrrhotite sphalerite and pyrite, with chalcopyrite.
-260	21.83	17.1							Banded iron formation with pyrite and chlorite.
-291	21.94	12.2					21.96	11.3	Coarse sphalerite veining pyrite.
401-196			21.86	15.8					Pyrrhotite containing specks of chalcopyrite.
-198			21.89	14.4	21.92	13.1			Coarse pyrrhotite and some chalcopyrite with qz. and siderite gangue.
308-316	21.85	16.2			21.88	14.9			Chalcopyrite veinlets in pyrrhotite.
-337	21.87	15.3			21.89	14.4			Chalcopyrite and pyrrhotite in pyrite.
-339			21.89	14.4					Massive pyrrhotite.
336-308					21.94	12.2	21.94	12.2	Coarse chalcopyrite and sphalerite assoc. with qz. veinlet.
381-544					21.88	14.9			Chalcopyrite veinlet in chlorite schist.
426-178	21.96	12.2					21.87	15.3	Massive pyrite with sphalerite and galena.
412-56	21.84	16.7							Massive pyrite.
368-165	21.84	16.7							
Mean	21.87	15.3	21.88	14.9	21.90	14.0	21.92	13.1	
Mean deviation	±.03	±1.3	±.01	±.4	±.02	±.9	±.02	±.9	

Standard No 2 22.21 δ^{34} = 0.0

TABLE IV

E ZONE SULFUR ISOTOPIC RATIOS

Sample No.	Pyrite		Pyrrhotite		Chalcopyrite		Sphalerite-galena		Description
	S^{32}/S^{34}	δ^{34}o/oo	S^{32}/S^{34}	δ^{34}o/oo	S^{32}/S^{34}	δ^{34}o/oo	S^{32}/S^{34}	δ^{34}o/oo	
D.H.376-734			21.83	17.1					Pyrrhotite bands in chlorite schist.
344-458A					21.93	12.6	21.91	13.5	Sphalerite, galena and chalcopyrite intimately mixed.
342-332	21.87	15.3	21.87	15.3					Pyrrhotite and pyrite.
387-748			21.89	14.4	21.88	14.9			Qz. vein with coarse chalcopyrite, pyrite, pyrrhotite.
344-427							21.83	17.1	Intimate mixture pyrrhotite, pyrite, chalcopyrite, sphalerite and galena.
362-496	21.92	13.1			21.94	12.2			Massive pyrite with pyrrhotite-chalcopyrite veinlet.
-503	21.95	11.7	21.95	11.7					As above.
362-523	22.02*	8.6					22.00*	9.5	Mixture of pyrite and magnetite with coarse sphalerite-galena and some chalcopyrite.
	(22.02)	(8.6)					(21.96)	(11.3)	
343-42	21.94	12.2			21.95	11.7			Mass. pyrite with chalcopyrite veinlet
348-153	21.91	13.5					21.91	13.5	Mass. pyrite with magnetite and sphalerite, galena.
-157	21.87	15.3			21.94	12.2			Mass. pyrite with magnetite and chalcopyrite.
357-368	21.87	15.3					21.88	14.9	Mass. pyrite with veinlet of sphalerite-galena.
351-123			21.89	14.4	21.92	13.1			Mass. pyrrhotite with a band of chalcopyrite.
-237	21.82	17.6			22.03	8.1			Pyrite veinlet in footwall porphyry.
345-68	21.94	12.2	____	____	22.03	8.1	____	____	Chalcopyrite veinlet in mixt. of pyrite and pyrrhotite.
Mean	21.91	13.5	21.89	14.4	21.94	12.2	21.91	13.5	
Mean deviation	±.04	±1.8	±.03	±1.4	±.02	±.9	±.04	±1.8	
Mean (less magnetite bearing samples)	21.90	14.0	21.89	14.4	21.93	12.6	21.88	14.9	
	±.04	±1.3	±.03	±1.4	±.02	±0.9	±.03	±1.2	

Standard No. 2 22.23 δ^{34} = -0.5

*Samples that contained abundant magnetite which breaks down to yield oxygen of different isotopic composition. In parentheses are values obtained after a crude separation with a horseshoe magnet.

(22.20 and 22.23) one in an acid tuff (22.14) and the other (22.23) in a peculiar soda-rich rock in the southeast part of the mapped area. The values for the basic rocks agree with those determined by Ault (3) of 22.02 to 22.26 while the values in the siliceous volcanic rocks lie close to meteoritic sulfur. These four values can then be considered to belong to syngenetic sulfides.

Nature of the Source.—The isotopic results indicate two important factors about the source:

(a) The narrow spread (8% of the total spread observed to date) indicates a uniform or well homogenized source.

(b) The ratios are all highly enriched in S^{34} relative to meteoritic sulfur which is regarded as the value of unfractionated earth (primordial) sulfur.

It is relevant at this stage to summarize the hypotheses regarding the origin of the New Brunswick ore deposits and decide which is most compatible with the isotopic results. There are three main hypotheses put forward for ore deposition.

A syngenetic origin postulates precipitation of the sulfides under reducing conditions during the deposition of the sediments (13). This is considered to be untenable as the sulfides of sedimentary origin generally show a broad

TABLE V

A ZONE SULFUR ISOTOPIC RATIOS

Sample No.	Pyrite		Pyrrhotite		Chalcopyrite		Sphalerite-galena		Description.
	S^{32}/S^{34}	$\delta^{34}o/oo$	S^{32}/S^{34}	$\delta^{34}o/oo$	S^{32}/S^{34}	$\delta^{34}o/oo$	S^{32}/S^{34}	$\delta^{34}o/oo$	
102-88						21.88	14.9		Chalcopyrite and pyrrhotite bands.
128-323			21.92	13.1	21.94	12.2			Coarse chalcopyrite and pyrrhotite with qz.
31-53	21.88	14.9					21.89	14.4	Mass. pyrite with carb. veinlet cont. sphalerite and galena.
Pyrite in vein	21.91	13.5							Pyrite in qz. vein in Hanging wall porphyry.
30-82	21.87	15.3							Pyrite-carbonate veinlet in sediment.
104-108	21.90	14.00					21.90	14.0	Sphalerite-galena in mass. pyrite.
105-73							21.88	14.9	Sphalerite-galena with dissem. pyrite.
Pyrite in foot w all	21.88	14.9							Pyrite dissem. in footwall chlorite schist.
107-232	21.86	15.8							Mass. pyrite with some chalcopyrite.
136-193			21.89	14.4					Mixt. of massive pyrrhotite and chalcopyrite.
-159	21.94	12.2					21.88	14.9	Sphalerite, galena carbonate vein in mass. pyrite.
-275					21.91	13.5			Pyrite, pyrrhotite, chalcopyrite vein in chlorite schist.
111-168	21.87	15.3							Pebbly pyrite dissem. in chlorite schist.
112-282							21.84	16.7	Mass. sphalerite.
-294			21.89	14.4	21.88	14.9			Chalcopyrite and pyrrhotite banded.
-296							21.88	14.9	Coarse sphalerite in Pb-Zn ore.
109-127	21.88	14.9	———	———	———	———	———	———	Massive pyrite.
Mean	21.88	14.9	21.90	14.0	21.91	13.5	21.88	14.9	
	±.02	±.9	±.01	±.5	±.02	±.9	±.01	±.5	

Standard No. 2 22.21 $\delta^{34} = 0.0$

TABLE VI

D ZONE SULFUR ISOTOPIC RATIOS

Sample No.	Pyrite		Pyrrhotite		Chalcopyrite		Sphalerite-galena		Description
	S^{32}/S^{34}	$34_{o/oo}$	S^{32}/S^{34}	$34_{o/oo}$	S^{32}/S^{34}	$34_{o/oo}$	S^{32}/S^{34}	$34_{o/oo}$	
230-394	21.92	13.1			21.91	13.5			Mass. pyrite cont. chalcopyrite.
-410	21.88	14.9	21.90	14.0					Mixt. of mass. pyrite and Pyrrhotite.
-452			21.90	14.0	21.91	13.5			Mass.pyrrhotite and chalcopyrite in chlorite schist.
222-245							21.89	14.4	Fine sphalerite and galena
235-65	21.89	14.4					21.90	14.0	Mass. pyrite with veinlet of sphalerite-galena.
212-157			21.92	13.1					Chalcopyrite in brecciated pyrrhotite.
-165							21.88	14.9	Intimate mixt. sphalerite, galena and qs.
206-99	21.90	14.0					21.97	10.8	Mass. pyrite with sphalerite veinlet.
-642	21.89	14.4							Mass. pyrite.
59-85			21.89	14.4	21.90	14.0			Coarse mixt. of chalcopyrite and pyrrhotite with some pyrite sphalerite, galena and qs.
204-161	21.88	14.9							Mass. pyrite.
-173					21.93	12.6			Mass. pyrite with chalcopyrite.
-545			21.87	15.3					Intimate mixt. of sphalerite, galena, chalcopyrite, and pyrrhotite.
238-519			21.88	14.9					Pyrrhotite in Qs. veinlet.
-535			21.87	15.1					Mass. pyrite with pyrrhotite;
Mean	21.89	14.4	21.88	14.9	21.91	13.5	21.91	13.5	
Mean deviation.	±.01	±.4	±.01	±.4	±.01	±.4	±.02	±.9	
Standard No.2		22.21	δ^{34} = 0.0						

spread of values. The sediments of New Brunswick are no exception and contain sulfides whose ratios range from 21.91 to 22.70 and average 22.31 (20).

A source bed origin postulates the sulfides formed syngenetically as above but that during later metamorphism these sulfides became mobilized and were transported through the source bed to be deposited in loci caused by favorable host rock (iron-rich sediments in this case) or zones of dilatancy. (Formed in this case by movement between the incompetent sediments and competent porphyry.) Knight (11) and Stanton (20) favor this, which conforms to Jensen's (10) metamorphic hydrothermal deposits.

A hydrothermal origin postulates ore-bearing solutions formed at depth from a cooling batholith, migrating upwards and forming ore deposits in much the same loci as above (Jensen's (10) magmatic hydrothermal type).

The application of the isotopic results can now be discussed further. The fact that the S^{32}/S^{34} ratios are enriched in S^{34} relative to meteoritic sulfur suggests a source rich in sulfate sulfur. Oceanic sulfates have a mean ratio of 21.76 and evaporite deposits of 21.80 (3). It is possible that such sulfates could have been trapped in sediments during deposition, either by absorption or simply by being caught up in pore spaces, or else evaporite deposits could have supplied the source of sulfate. However, sulfates are not easily reduced

TABLE VII

SULFUR ISOTOPIC RATIOS IN COUNTRY ROCKS

Sample No.	Description	S^{32}/S^{34}	δ^{34} o/oo
S 16	Fine grained dark tuff containing disseminated Pyrite.	22.14	3.2
S 17	White soda rich flow (?) rock containing abundant disseminated pyrite.	22.23	−0.9
S 20	Siliceous volcanic close to B-2 ore zone, and containing some pyrite.	21.94	12.2
S 22	Siliceous volcanic containing pyrite.	21.96	11.3
R.R.	Siliceous volcanic containing pyrite.	21.97	10.8
S 24	Siliceous volcanic interbedded in basic types.	21.88	14.9
S 28	Siliceous volcanic, highly sheared.	21.97	10.8
S 30	Quartz-felspar porphyry containing coarse disseminated pyrite, obtained from near station.	21.98	10.4
S 32	Quartz-felspar porphyry containing sulfide in B-2 zone.	22.03	8.1
340–255′	Disseminated sulfide in porphyry in B-2 zone.	21.98	10.4
350–118′	Disseminated sulfide in porphyry in B-2 zone.	21.78	19.4
S 25	Basic volcanic rock containing pyrite and pyrrhotite.	22.23	−0.9
S 26	Basic volcanic containing pyrite and pyrrhotite	21.78	19.4
S 2	Basic volcanic containing pyrite and pyrrhotite	22.20	0.5
S 5	Quartz "eye" sediment.	22.01	9.0
S 4	Fine chlorite rock containing coarse pyrite.	22.04	7.7
S 12	Quartz "eye" rock with quartz veins and pyrite; unlikely syngenetic	21.84	16.7
S 29	Sulfide disseminated in chloritic rock in B-2 zone.	21.99	9.9
429–260′	Pyrite and chloritic material in iron formation.	21.83	17.1
58–89	Pyrite in pink gneissic granite	21.84	16.7
58–91	Pyrite in pink gneissic granite.	21.99	9.9

to sulfides except in the presence of carbon at temperatures above 600° C. It is postulated that organic carbon present in the sediments was responsible for this reduction. Evidence that this reaction is possible is the presence of graphite in mineralogical specimens and carbon dioxide (up to 15%) in the sulfur dioxide analyzed on the mass spectrometer. Graphite is a common accessory mineral in the Brunswick Mining and Smelting ore as well (11, 1), and generally throughout the district. It is considered to be excess carbon remaining after the reduction has taken place. However, the temperatures at which this reaction is possible are higher than those expected from the regional metamorphism (albite-epidote grade of the greenschist facies) but close to those estimated for ore deposition, (555° to 605° C, by Benson (4) and 515° to 550° C, by Arnold (2)), so that the most favorable place for the reduction to occur is at depth during the creation of a magma or during the process of granitization, from which the ore-bearing solutions could be expelled.

The narrow spread in ratio values not only for Heath Steele, but for all the New Brunswick massive sulfide bodies (21) is best interpreted on the basis of a deep-seated homogeneous source. An interesting calculation can be made about the temperature of this source. If it is assumed that the sulfide bodies are derived from a rock containing both sulfide (higher ratio) and sulfate (low ratio), then as this rock is forced down in the keel of a

geosyncline the temperature will gradually be raised so that the enrichment factors, assuming equilibrium conditions, for the exchange reaction:

$$S^{34}O_4'' + S''^{32} \rightleftharpoons S^{32}O_4'' + S''^{34}$$

will approach unity as follows (16).

At 100° C Fractionation factor = 1.058.
At 500° C Fractionation factor = 1.016.
At 700° C Fractionation factor = 1.010.
At 900° C Fractionation factor = 1.006.

If it is then assumed that the lowest ratio present in the ore is formed from original sulfate and the highest ratio from original sulfide, then an enrichment factor (fractionation factor) can be obtained for the Heath Steele sulfides:

$$\frac{S^{34}/S^{32} \text{ in sulfate}}{S^{34}/S^{32} \text{ in sulfide}} = \frac{0.045829}{0.045413} = 1.009.$$

As equilibrium conditions were very unlikely it is possibly fortuitous that this indicates a temperature between 700° and 800° C or about the temperature at which large scale reduction of sulfate would occur, and prevent further exchange and homogenization.

The sulfur isotopic results show a relationship between the ore bodies and the granites. Thus the ratios of the sulfides found in the gneissic granite (21.99 and 21.84) close to Heath Steele lie within the ore range (21.82–22.02), and the ratios of the sulfides in the intrusive granites in the Bathurst area (22.13 and 22.24) are within the ore zone range of the fissure deposits in the Silurian rocks of 21.90–22.22 (20). It is possible that the differences between the massive sulfide deposits in Ordovician rocks and the fissure deposits in Silurian rocks can be accounted for by variations in the relative amounts of sulfate and sulfide in the source rocks, or possibly a change in the ratio of the ocean from which the sulfate was derived.

CONCLUSIONS

It appears then that a magmatic hydrothermal origin is most favored by the isotopic results. However, it must be admitted that all the writer has done is to take a source bed and bury it until suitable temperatures are reached to cause reduction of the sulfates, mobilization of the resulting sulfides, and granitization of the original rock. The source of metallic ions is easily found in a volcanic provence such as must have existed during the Ordovician, and could have been added to the ocean basin in many ways to be trapped in the source rock along with the sulfate.

YALE UNIVERSITY,
NEW HAVEN, CONN.,
July 20, 1959

Present address:
RHODESIAN SELECTION TRUST MINE SERVICES LTD.
NORTHERN RHODESIA

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COMPOSITIONAL VARIATION OF ALKALI FELDSPARS IN SOME INTRUSIVE ROCKS NEAR GLOBE–MIAMI, ARIZONA

FREDERICK J. KUELLMER

ABSTRACT

Approximate compositional determinations were made by means of X-ray study of the ($\bar{2}01$) spacings of heated alkali feldspars. Of 32 alkali feldspar specimens from the Lost Gulch quartz monzonite, 17 from within the areas of moderate hydrothermal alteration average 93 weight percent orthoclase (Or/Or + Ab + An), whereas the remaining specimens, from outside the moderately altered areas, contain only 83 weight percent orthoclase. Likewise, alkali feldspar specimens (7) from within the moderately altered area near the Inspiration lobe of the Schultze granite have an average bulk composition of Or_{88}, and Schultze granite and Inspiration-lobe feldspar specimens (21) from outside the area of moderate alteration have an average bulk composition of only Or_{78}. Primary magmatic crystallization differentiation, or hydrothermal crystallization or recrystallization appears to be a plausible hypothesis to explain these compositional differences. Such compositional variations suggest again a genetic relationship between magmatic crystallization and ore concentration.

INTRODUCTION

RECENT studies of alkali feldspars by Bowen, Goldsmith, Laves, MacKenzie, J. V. Smith, and Tuttle have shown considerable structural and compositional variation. Most orthoclase feldspars are perthitic on some scale ranging from microscopic to X-ray and possibly even finer. The two phases comprising perthitic feldspars, one potassium-rich and the other albitic, may be made homogeneous by adequate heat treatment and the resulting homogeneous feldspar composition can be determined by X-ray measurement of the lattice spacings.

In the Cordilleran region, there are abundant shallow-depth Tertiary and Cretaceous granitic rocks, many of which are intimately associated with ore deposits (2, 4, 5). Many of these rocks contain, as a conspicuous constituent, large optically homogeneous alkali feldspars which, on the basis of the recent feldspar studies, probably are cryptoperthites. In addition, in the ore districts, alkali feldspars occur as alteration products or as hydrothermal minerals (11, p. 168).

As a result of study of alkali feldspars in a great many porphyries of the Southwestern United States, it is apparent that feldspars show considerable compositional and structural variation even in small homogeneous intrusives, and that such variation in many cases is not independent of the protore distribution (3). Data presented here show what is believed to be a noteworthy

variation in alkali feldspar composition correlative with known areas of moderate hydrothermal alteration in the Globe-Miami area of Arizona.

Detailed geologic studies by Peterson (7, 8, 9, 10) demonstrate that the sequence of intrusives from which samples have been obtained is as follows: Lost Gulch quartz monzonite, the oldest, followed by the granite porphyry and the Schultze granite, both of approximately the same age. The granite porphyry, which is included with the Schultze granite in Figure 1, occurs predominantly along the margins of the Schultze granite near the Inspiration-Miami mining area and may represent only a contact facies of the granite. Tentatively, the intrusives are believed to be of Late Cretaceous or Early Tertiary age (8, p. 124). Soon after the intrusions, extensive copper mineralization took place. All the geologic data, other than the feldspar compositions shown in Figure 1, are copied from Peterson's published studies.

Within each of the three areas of moderate hydrothermal alteration (outlined in Fig. 1), there are major copper-producing mines: (1) the Copper Cities mine, the northernmost; (2) the Castle Dome mine, the westernmost; and (3) the Miami-Inspiration mines, closest to the city of Miami. This does not imply that all the alteration within these areas is only moderate, or that secondary enrichment was not important in producing ore. For additional petrographic and structural details, the reader should consult Peterson's studies, cited above.

PROCEDURE

Large hand specimens of the granitic intrusives were obtained throughout the area and their locations plotted on topographic maps, following the advice and suggestions of Peterson and with the generous assistance of mining company officials. Fresh alkali feldspars were handpicked from the igneous rocks, which are predominantly coarse grained and porphyritic, with careful and repeated sorting of feldspar material. For some of the specimens, the preliminary picking and sorting were followed by heavy-liquid separation. Feldspar compositions, given in Figure 1 in the weight percent of the orthoclase ($KAlSi_3O_8$) content of the total orthoclase-albite-anorthite composition, were determined by measuring the $(\bar{2}01)$ spacing of the heated alkali feldspars (12, p. 10). Feldspar samples ground to less than 325 mesh were heated to 1,050° C for at least 48 hours. According to Orville (6, p. 208), although dry heat treatment of this nature is not sufficient to sanidinize the perthitic feldspars, sufficient homogenization takes place so that the $(\bar{2}01)$ reflection can be used as an indicator of composition. This was verified by heating various artificial mixtures of spectrographically analyzed sanidine, microcline, and albite. In general, the spectrographic analyses are 7 weight percent or less lower in orthoclase content. Both sets of data are consistent except for three determinations. Such a difference might be expected as a consequence of the accuracy of the spectrographic analyses, the accuracy of the $(\bar{2}01)$ position as a composition indicator, and the nature of the analytical methods; i.e., the spectrograph would determine the Na and Ca content of the plagioclase phase of the perthite as well as of any inclusions of foreign plagioclase, whereas

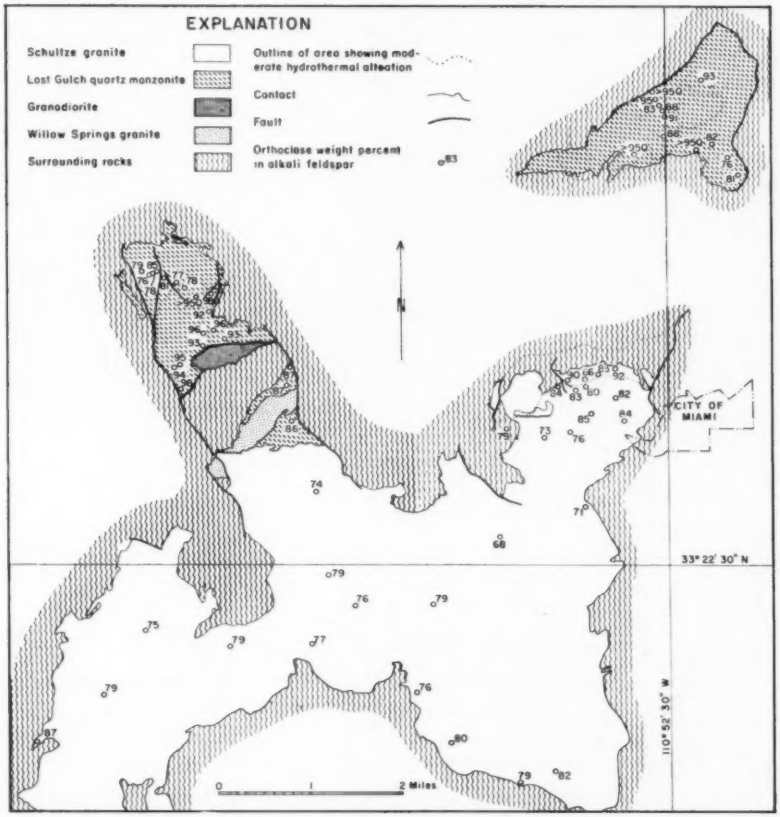

FIG. 1. Outline geologic map of the Lost Gulch quartz monzonite and the Schultze granite, taken from Peterson's data (7, 8, 9, 10), and showing compositional variation of the alkali feldspars. See text.

heat treatment of plagioclase inclusions might not noticeably affect the $(\bar{2}01)$ composition determination. For the above reasons, the orthoclase weight percentages in the alkali feldspars are believed accurate to within a minus 7 percent. The $(\bar{2}01)$ spacings were measured with a Norelco high-angle goniometer diffractometer, using internal standards ($KBrO_3$; in some of the earlier runs, $NH_4H_2PO_4$), and were measured to 0.005° of 2θ for nickel-filtered copper radiation. The feldspar bulk compositions are plotted in Figure 1 near a small circle indicating the sample locality. Five specimens from the Lost Gulch quartz monzonite showed a small quartz $(10\bar{1}0)$ reflection after the heat treatment, which remained in spite of numerous attempts to obtain a purer sample, so that the bulk composition could be determined only

as greater than about 95 weight percent orthoclase. In Figure 1, these estimated compositions are indicated by the symbol > 95Q, and in Figure 2, by the black dots.

RESULTS

For each rock unit, specimens from in or close to the areas of moderate hydrothermal alteration, as outlined by Peterson, contained a significantly greater $KAlSi_3O_8$ content than the orthoclase feldspar samples obtained outside these areas. The Lost Gulch quartz monzonite specimens, 32 in number, have an average bulk composition within the ore areas (which here means areas of moderate hydrothermal alteration) of 93 weight percent orthoclase, and outside the ore areas an average composition of 83 weight percent. The Schultze granite feldspars, including those from the granite porphyry of the Inspiration lobe, on the basis of 28 specimens, have an average bulk composition of 85 weight percent orthoclase in the ore areas, and an average bulk

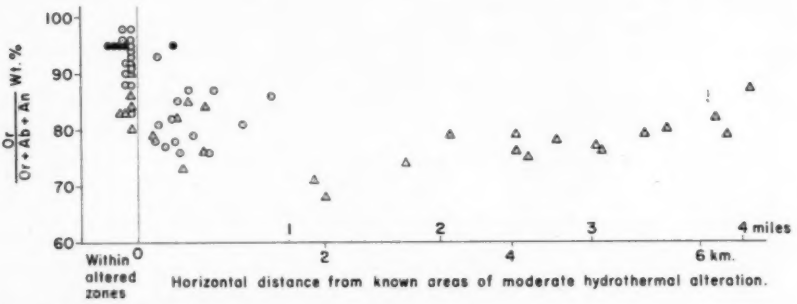

FIG. 2. Compositional variation of alkali feldspars within the altered zones and as a function of distance from the nearest edge of a moderately altered area.

composition elsewhere of 78 weight percent. From visual inspection of Figures 1 and 2, and from the statistical summary in Table 1, it is apparent that these differences are significant and probably of importance for igneous petrology as well as for ore distribution and genesis. The average bulk composition of the Schultze granite and Inspiration lobe samples is 80 weight percent orthoclase ($KAlSi_3O_8$), and for the Lost Gulch quartz monzonite 88 weight percent, in the orthoclase feldspars.

Preliminary X-ray diffractometer studies, during heat treatment to about 700° C, demonstrate that the perthitic orthoclase feldspars (perthitic on an X-ray scale) from the ore areas remix and become homogeneous more completely and sooner than feldspars from the nonore areas, with the possible exception of the specimens from the Castle Dome mining area and surroundings. Four feldspar specimens from the Lost Gulch quartz monzonite mass near the Castle Dome mining area all remix very readily, so that the slight

TABLE 1

STATISTICAL SUMMARY OF THE COMPOSITIONAL DATA*

	Number of samples	Mean Or %	S.D.	Difference of means	S.D. of means
Lost Gulch qz. monz.					
altered area	17	93	3.97	10	1.82
non-altered area	15	83	5.97		
Inspiration lobe and Schultze granite					
altered area	7	85	4.27	7	1.89
non-altered area	21	78	4.56		

* S.D. refers to the standard deviation. The fact that the difference of the means is more than five times greater, in one case, and nearly four times greater, in the second than the standard deviation of the means, makes it highly unlikely that the compositional differences could be the result of random sampling of a single compositional group.

differences may not be real in this case. Such rapid remixing suggests a higher temperature state for orthoclase feldspars within the areas of moderate hydrothermal alteration. However, additional study, now in progress, is necessary in order to substantiate this suggestion.

INTERPRETATION

The difference in average bulk composition of orthoclase feldspars from the Lost Gulch quartz monzonite and from the Schultze granite and Inspiration lobe samples, on the basis of study of laboratory systems (12) and the known relative ages of these rocks, provides additional evidence favorable to a comagmatic origin by means of fractional crystallization for these intrusives (7, 8, 9, 10).

Two hypotheses concerning the origin and significance of the alkali feldspar compositional variations are considered here, without extensive review of magmatic differentiation, ore genesis, hydrothermal alteration, and ore-forming fluids, which have been adequately treated elsewhere (1, 2, 4, 5, 11). First, are these compositional differences the result of primary crystallization differentiation, or second, are they the result of a secondary compositional adjustment of primary crystals during a hydrothermal stage in addition to crystallization during the hydrothermal stage?

The suggestion that the orthoclase feldspars from within the ore areas are in a higher temperature state than those from the surrounding areas applies equally well to both hypotheses. As the potash-rich phases should crystallize first and at a higher temperature from a potassic feldspar melt (12), the first hypothesis is tenable. The slight differences in the rate and ease of remixing or homogenization for feldspars from the Lost Gulch quartz monzonite near the Castle Dome area provide additional evidence that these compositional variations are primary. However, with rapid crystallization, in accordance with Ostwald's law, it is also possible that the higher temperature state of the orthoclase feldspar might form metastably at a lower temperature in the hydrothermal range.

One might also ask why a relationship should exist between early formed

higher temperature potash feldspars and a very late ore-forming fluid or hydrothermal stage. An explanatory model known for many years (1, 2, 4, 5) might be as follows: 1. During magmatic crystallization the residual fluid becomes enriched in volatiles. 2. Ultimately the volatile pressures may exceed the confining pressure and fracture the surrounding rock. Such volatiles may or may not transport ore-forming materials, and may or may not alter rocks. 3. That part of the surrounding rock which fractures must be solid, or brittle enough to be broken. 4. The earliest formed part of the crystallizing igneous rock might be solid or brittle enough to be fractured by the time the volatile content in the residual fluid was great enough to brecciate its surroundings.

For the present, sufficient data are not available to evaluate the foregoing hypotheses adequately. The data show, however, that considerable mineralogic variation may exist even within homogeneous igneous rocks. Also, the data provide increased support for the idea of a genetic relationship between magmatic crystallization and ore concentration.

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NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY,
SOCORRO, NEW MEXICO,
July 20, 1959

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LITHOLOGIC CLASSIFICATION OF TACONITE FROM THE TYPE LOCALITY [1]

JAMES NOVOTNY GUNDERSEN

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ABSTRACT

The Biwabik iron-formation in the Eastern Mesabi district, the type locality for taconite, consists of interbedded strata of two fundamental or basic types, namely massive and thinly bedded. The most significant difference between the various taconite rock types is merely the relative abundance and mineralogy of these two types of strata. On this basis, five general groups of taconite are proposed. The assignment of a specific rock name to a given rock type, such that it clearly indicates the mineralogy and relative abundance of each of the two kinds of strata, is impossible by use of conventional classification methods. Consequently, a simple, although somewhat unorthodox, classification scheme is proposed and is illustrated.

INTRODUCTION

ALTHOUGH the Biwabik iron-formation in the Eastern Mesabi district, the type locality for taconite, has been substantially metamorphosed, its relic sedimentary stratification is apparent almost everywhere. The rocks of the iron formation can be classified according to a number of generalized classifications depending upon the purpose for naming these chemical sediments. Most of the iron formation throughout the entire Mesabi range consists primarily of four main mineral groups: quartz (and chert), iron-rich silicates and carbonates, and iron oxides. The gross mineralogy of the Eastern Mesabi district is simple, consisting essentially of magnetite, quartz (and chert), and iron-rich silicates. On the Main Mesabi range most of the silicates are minnesotaite,

[1] Publication authorized by the Director, Minnesota Geological Survey.

stilpnomelane, and greenalite, all of which are difficult to recognize in hand specimen because of their fine grain size. The most abundant silicates found at the type locality are cummingtonite, ferrohypersthene, fayalite and lesser amounts of calcium-bearing ferrous silicates, all of which are commonly sufficiently coarse grained to be recognized with the hand lens. In the general classification presented below, silicates are considered as a group but where recognized the appropriate mineral name should be used in naming a specific rock type.

The fact that any of the minerals of the taconites from the type locality can occur in any of a variety of relic sedimentary structures, and that within each of these structures, can vary in abundance from near zero to nearly 100 percent, greatly complicates the task of lithologic classification. For example, a "magnetite-silicate-quartz rock" can refer equally well to a homogeneous rock containing all three minerals; or a rock containing layers of magnetite and of silicate and quartz; or clusters of grains of magnetite and silicate in a quartz rock; or numerous other possibilities. Results of beneficiation tests also indicate that the concentrating characteristics of the magnetic taconites are closely related to the general type under consideration. The wide variety of rock types of somewhat similar mineralogy make it apparent that a workable, yet detailed, classification is needed for the Eastern Mesabi taconites to help predict their beneficiation characteristics, as well as to aid in the recognition and unique description of the numerous stratigraphic units of the formation.

The classification of Mesabi range taconites in general has been discussed by Gruner (2, p. 32) and recently by White (7, p. 7). Gruner's classification is simple and easy to apply, but as far as the rocks on the Eastern Mesabi range are concerned, his scheme is too inclusive to be distinctive. White's classification is more complicated and is difficult to apply to the rocks of the type locality.

The writer's classification of the Biwabik iron-formation taconites is essentially an expanded but more specific version of Gruner's scheme and it also takes advantage of some of the useful concepts employed by White. It is based upon the features actually present in the rock and not upon the absence of certain features. It is consistent regardless of the mode of examination of the rock such that additional information attained by microscopic study will merely augment the rock name but will not change the basic taconite name.

This classification was developed during a study of the stratigraphy and mineralogy of the taconites at the type locality (3). This work was supported by two Reserve Mining Company research fellowships, for the years 1955 to 1957, at the University of Minnesota and by the Minnesota Geological Survey, Dr. G. M. Schwartz, Director.

USE OF THE WORD TACONITE

Gruner (2, p. 7) states: "The earliest descriptions of taconite were from the East Mesabi district . . . the part of the (Mesabi) range east of Mesaba.

. . ." Davis (1, p. 282) presents an interesting review of the name taconite. The first step in the development of the name 'taconite' was made by N. H. and H. V. Winchell (9, p. 113) who made the mistaken correlation of the rocks of the Biwabik and Gunflint iron formations as being of Taconic (Lower Cambrian) age. H. V. Winchell (8, p. 124) first uses the word *taconyte* as a rock name to describe certain basal parts of the iron formation on the Mesabi Range and shortly afterwards, Spurr (6, p. 248) used the word for any iron-bearing rock. Near the turn of the century, the spelling became firmly established as 'taconite.' Through common usage, the word taconite has since been extended to include all rocks of the Biwabik iron formation except the oxidized ores (2, p. 5).

Taconite has also been used colloquially as a rock name to describe the rocks from other stratified Precambrian sedimentary iron-formations of the world, although other names such as 'iron-formation' have been specifically used as rock names. Because there are probably few iron formations of the world that are metamorphosed to the extent of the rocks of the Eastern Mesabi district, it would seem that few are sufficiently similar petographically to those at this type locality to warrant the rock name taconite. It is not the purpose of this paper, however, to discuss to what rocks outside the type locality the rock name taconite should be applied. The rock name has proven so useful that it would be virtually impossible to restrict the name to the rocks of the Eastern Mesabi Range. The writer agrees that the manner in which Gruner (2) has employed the term seems best suited to name the rocks of stratified Precambrian iron-formations that contain significant amounts of iron-bearing silicates, carbonates, and oxides without restrictions as to whether the rocks are sediments or metasediments, or if they are fresh or partially oxidized. In the following text, the word taconite will be used in a general sense in describing the rocks of the iron formation but when it is used as a rock name it will be written *taconite*.

DEFINITION OF TERMS

The Biwabik and other similarly stratified iron formations have consistently been called, and probably will continue to be called, "banded iron formations." Everyone recognizes that these stratified formations have only a "banded structure," which is apparent when looking at the stratification in cross section in an outcrop or in a core specimen. Many use the word "band," a two-dimensional surface, when they mean to use layer or bed, a three-dimensional tabular body. Consequently, the words "bands," "banded," and "banding" are not used in the proposed classification.

There are no slates, rocks possessing slaty cleavage or the implied composition, among the metamorphosed iron formation rocks at the type locality. Similarly, geologists have recognized the fact that there are no slates among the rocks of the Biwabik formation in other parts of the Mesabi range. Nevertheless, the words "slate" and "slaty" are persistently used, merely to indicate the dominance of thin beds, despite the fact that the connotations concerning structure and composition usually connected with these words do not

apply. In the present classification, words other than slaty will be employed to indicate the presence and abundance of thin-bedded strata within the formation.

There seems little doubt that nearly all of the quartzose layers of the iron formation once consisted of fine-grained silica, probably chert. If the definition of chert is restricted to amorphous chalcedony and crypto-crystalline quartz, then chert is rare in the Eastern Mesabi district. As a compromise to avoid losing the use of two useful mineral names, bedded silica that is easily resolvable with a 10 × hand lens as distinct grains (mostly about 0.1 mm diameter) is called quartz and more finely crystalline or microcrystalline quartzose material is called chert.

STRATIFICATION STRUCTURE OF TACONITE

The Biwabik iron-formation on the Eastern Mesabi range consists mainly of two distinctly different kinds of strata, here defined as *bedded taconite-strata* and *massive taconite-strata,* that are interbedded to form almost all of the iron formation. Both kinds of strata are schematically illustrated in Figure 1. Although both types of strata are bedded in the true sense of the word, bedded taconite-strata includes the beds that are responsible for the obvious layered or stratified aspect of the formation. These beds generally contain most of the iron oxides of the formation, although there are important

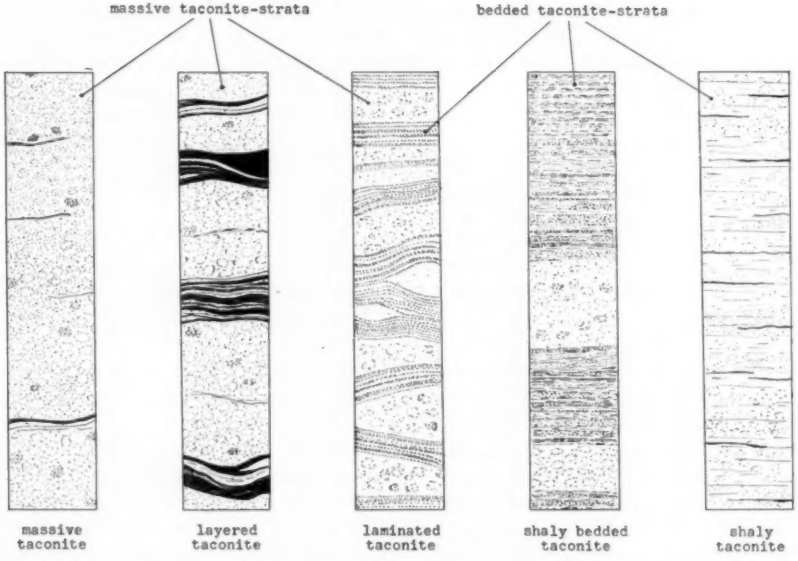

FIG. 1. Simplified sketches of the five general types of taconite, showing generalized distribution of bedded and massive taconite-strata.

exceptions. All of the "bands" and many of the "slaty beds" of older classifications correspond to this type. In contrast, massive taconite-strata are the layers or beds that are massive in the sense that they are normally devoid of any internal stratification. These strata would include the massive layers of "silicate taconite" and "cherty taconite" of existing schemes. Both types of strata may range in thickness from almost zero to several meters but the great majority of individual layers are less than 15 cm.

In most instances, the most apparent difference between the rock types of the formation is the average thickness and abundance of one kind of strata relative to the other. This significant feature is the ultimate basis for naming the general types of taconite.

CLASSIFICATION OF TACONITE

Five general types of taconite are proposed in this classification, depending upon the relative abundance of the bedded taconite-strata that are interbedded with massive taconite-strata. By definition, these types are:

Type 1: *massive taconite* consists almost entirely of massive taconite-strata with from zero to about 10 percent by volume of bedded taconite-strata.

Type 2: *layered taconite* consists primarily of massive taconite-strata interbedded with about 10 to 40 percent by volume of bedded taconite-strata.

Type 3: *laminated taconite* contains about 40 to 60 percent by volume of bedded taconite-strata with the balance consisting of massive taconite-strata.

Type 4: *shaly bedded taconite* contains about 60 to 90 percent by volume of bedded taconite-strata with massive taconite-strata composing the rest.

Type 5: *shaly taconite* consists almost entirely of bedded taconite-strata with from zero to about 10 percent by volume of massive taconite strata.

It is clear from the above definitions that words connotating structural features are incorporated into the general rock names, as has been done in other taconite classifications, e.g. "banded taconite." Unfortunately, these words are not mutually exclusive because, for example, the shaly bedded rocks are certainly both laminated and layered. The particular structural prefixes were selected to best distinguish among the general bedding features shown by the rocks. Therefore they must be recognized only as convenient comparative prefixes used to designate a particular general group of taconites.

Briefly, the mineralogy of the massive taconite-strata determines the basic rock name of the specific taconite types. The mineralogy of the bedded taconite-strata is also incorporated into the rock name by means of parentheses immediately following the structural prefix portion of the rock name, as explained in later sections. Petrologists may have valid objections to such

TABLE 1

General *taconite* types	Volume percent of bedded taconite-strata	Specific *taconite* rock names
1. *massive taconite*	0 to 10	*C–D taconite*
2. *layered taconite*	10 to 40	*layered (A–B) C–D taconite*
3. *laminated taconite*	40 to 60	*laminated (A–B) C–D taconite*
4. *shaly bedded taconite*	60 to 90	*shaly bedded (A–B) C–D taconite*
5. *shaly taconite*	90 to 100	*shaly A–B taconite*

composite rock names but there seems to be no alternative for rocks as complex as taconites.

The general scheme of classification is summarized in Table 1 and is illustrated in Figure 1. Without being specific, assuming that the mineralogy of the massive taconite-strata consists dominantly of mineral D and lesser amounts of mineral C, and similarly, that the bedded taconite-strata consists mainly of mineral B and lesser amounts of mineral A, then Table 1 also shows the simple scheme used in naming the specific *taconite types*. In general, the mineralogical compositions of the most common varieties of massive, and bedded, taconite-strata are as shown in Figure 2a.

At this point, it is clear that a systematic method is necessary for stating mineralogy of the massive taconite-strata that is to be used as the root name

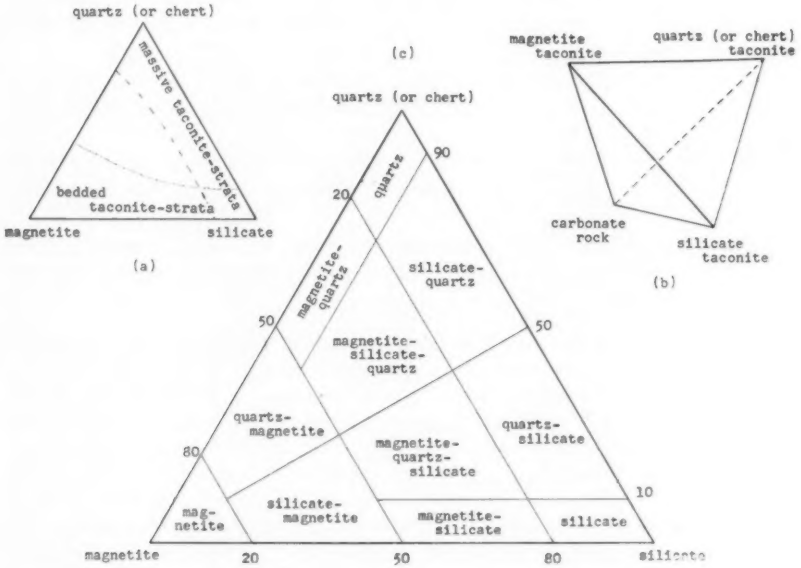

FIG. 2. Mineralogical varieties of taconite. Diagram (a) shows the most common range in mineral composition of massive and bedded taconite-strata. Diagrams (b) and (c) designate the mineralogical varieties of *massive taconite* and massive taconite-strata.

of the specific rock name, i.e. *C-D taconite* in the abstract examples listed above. By definition, this method is identical to that proposed for the mineralogical subdivision of the general class of *massive taconite,* Type 1, presented below. Details of forming the specific rock names of each of the general taconite types is discussed in the following sections.

Type 1: Massive Taconite.—The rock name *massive taconite* includes a general class of taconites that consist of massive taconite-strata and similar rocks containing up to 10 percent by volume of bedded taconite-strata; consequently, these rocks show little or minor internal stratification, but they commonly contain abundant granule structures. In general, other internal structures are not sufficiently significant or abundant to be included in the specific rock name, but a few exceptions are discussed at the end of the paper.

Designation of the mineralogical subdivisions of *massive taconite* is facilitated by the use of the end-member concept proposed by Pettijohn (5, p. 187). A concise discussion of the use of the fundamental tetrahedron in end-member classifications is presented by Krumbein and Sloss (4, p. 115). Depending upon their mineralogical composition (assuming 100 percent end-members), the four possible basic varieties of massive taconite are indicated in Figure 2b.

Because of the absence of *carbonate rock,* especially of the siderite-rich rock that occurs on the Main Mesabi range, all of the intermediate varieties of *massive taconite* occurring in the Eastern Mesabi district lie in the magnetite-quartz-silicate plane of the tetrahedral diagram. This plane is redrawn as Figure 2c. The varieties that are intermediate to the end-member types have been divided on the basis of arbitrary limits which are convenient for differentiating among the Eastern Mesabi taconites.

In applying a rock name to a specific variety of this general taconite group the mineralogical prefix indicated in Figure 2c is substituted for the word "massive"; for example, *silicate-quartz taconite* if the mineralogy of the rock lies in the silicate-quartz "field" of the diagram.

The most abundant varieties lie between the *quartz taconite* and *silicate taconite* end-member types and can contain up to 20 percent by volume of disseminated magnetite or magnetite in granules. *Massive taconites* containing between 20 and 50 percent by volume of magnetite are encountered locally but those containing more than 50 percent of magnetite by volume are rare.

Type 2: Layered Taconite.—Use of the rock name *layered taconite* defines a general group of rocks containing 10 to 40 percent by volume of bedded taconite-strata interstratified with massive taconite-strata without any designation as to the mineralogy of the rock.

The bedded taconite-strata of this group consist dominantly of magnetite-rich layers and lamellae that commonly show a variety of thicknesses, as well as groups of these beds. Most of the individual layers range from 1 mm to 2 cm but groups of layers commonly reach 4 to 5 cm in thickness. The interstratified massive taconite-strata normally range from about $\frac{1}{2}$ to 20 times the average thickness of the magnetite-rich layers but are mostly about ten times as thick.

Upon recognition of the mineralogy of each of the strata types, specific rock names for this second general type of taconite can be made according to the scheme previously outlined. For example, if the bedded taconite-strata consists of magnetite with subordinate amounts of silicate, and the mineralogy of the massive taconite-strata lies within the quartz "field" of Figure 2c, then the specific rock name is *layered (silicate-magnetite) quartz taconite.*

All of the above mentioned general and specific rock names are defined to contain mostly bedded taconite-strata that have well- and regularly-bedded layers, generally of uniform thickness. Many types of rock belonging to this class, however, are rather irregularly bedded and commonly contain lenticular layers that locally split and join other layers. Where appropriate, and necessary for detailed logging or description, this general variety of layered taconite is described as *wavy layered taconite,* which is of course subject to more detailed mineralogical designation according to the scheme described above.

Type 3: Laminated Taconite.—The rock name *laminated taconite* designates a general class of rocks that contain 40 to 60 percent by volume of bedded taconite-strata with the balance consisting of massive taconite-strata but does not indicate the mineralogy of the rocks.

The bedded taconite-strata of this group typically consist of laminated zones of closely-spaced, magnetite-bearing lamellae that tend to be of nearly equal thickness, normally averaging from about 0.5 to 2 mm in thickness. The laminated zones commonly contain significant amounts of quartz (or chert) and silicates, and they generally range in thickness from 1 to 15 cm but most of them are less than 5 cm.

Specific rock names for this general group of taconite are obtained in the manner outlined in the previous section. Therefore, if the bedded taconite-strata consisted mainly of magnetite and some silicate interbedded with massive taconite-strata of chert, the specific rock name is *laminated (silicate-magnetite) chert taconite.*

The laminated zones of this group of rocks are implied to be regularly bedded and of fairly uniform thickness. In some places, however, the laminated zones are somewhat irregularly bedded and locally less uniform in thickness and the general rock name *wavy laminated taconite* is suitable in these cases.

Type 4: Shaly Bedded Taconite.—The rock name *shaly bedded taconite* defines a general group of rocks that consists of 60 to 90 percent by volume of bedded taconite-strata interstratified with subordinate amounts of massive taconite-strata, without designation of the mineralogy. Rocks consisting of more than 80 percent of magnetite-bearing bedded taconite-strata are uncommon on the Eastern Mesabi range.

There is a great deal of difficulty in selecting a lithologically correct name to describe the abundance of thin beds and lamellae throughout this group of rocks. The magnetite in the bedded taconite-strata is sparsely disseminated within uniform lamellar layers, averaging 1 to 2 mm thick, along with significant amounts of quartz and silicates. These thin beds are typically inter-

layered with quartz- and silicate-rich lamellae of similar thickness to form collectively laminated zones that range in thickness from 1 to 60 cm, most of which are less than 15 cm. Consequently, these abundant bedded taconite-strata are similar in their stratification structure to a shale; hence, the structural prefix "shaly bedded" in the rock name. It must be emphasized that the taconites of the Biwabik iron-formation are not even remotely similar to shales in composition, nor do they possess a shaly structure or parting. The phrase, shaly bedded, is used merely as an allusive prefix to distinguish it from other varieties of stratified iron formation. The interstratified massive taconite-strata are mostly from 1/20 to 2 times the average thickness of the laminated zones of bedded taconite-strata.

The naming of specific varieties of this group of taconites is identical to the scheme followed in the earlier sections. For instance, *shaly bedded (magnetite-silicate) quartz taconite* indicates a taconite of this type that contains bedded taconite-strata consisting of silicate and some magnetite and massive taconite-strata consisting of quartz. In the Eastern Mesabi district, the bedded taconite-strata are nearly always regularly bedded and uniform in thickness and, therefore, "wavy bedded" varieties are not common.

Type 5: Shaly Taconite.—The rock name *shaly taconite* defines a general group of taconites that consist of bedded taconite-strata and similar rocks containing up to 10 percent by volume of massive taconite-strata.

The stratification of this group of rocks is rarely as pronounced as in the preceding three general types of taconite because of the normal lack of magnetite-rich beds and lamellae. *Shaly taconite* is perhaps best visualized as a special variety of silicate-rich *massive taconite* that has a distinct thin-bedded aspect despite the absence of magnetite-rich layers and lamellae. There is sufficient segregation of silicate, quartz and locally graphitic material into somewhat concentrated, yet diffuse, regularly-bedded lamellae and thin layers to produce the overall shaly aspect throughout the rock. Because of the lack of distinct layers that are appreciably different mineralogically from their surroundings, the usual naming method of placing the dominant mineralogy of the bedded taconite-strata in parentheses is not applicable. Instead, this general type of taconite is mineralogically classified in the same manner as *massive taconite*, according to Figure 2c, and the structural prefix "shaly" replaces "massive" in naming the general taconite type. In naming a specific taconite type of this group, the prefix "shaly" is retained to distinguish it from mineralogically similar types. Therefore, *shaly quartz-silicate taconite* defines a rock that has a mineralogical composition that lies in the quartz-silicate "field" of Figure 2c, but which also is distinctly internally stratified throughout. In detailed logging of core, the general rock name *magnetic shaly taconite* was found to be useful in noting thin zones in the rock that were somewhat richer in magnetite.

SPECIAL TACONITE TYPES

Certain internal structural features occurring within massive taconite-strata constitute unique rock types. The rock naming scheme for these types again

employs a word that alludes to the structural feature, as a prefix to the basic rock name and is again followed by parentheses enclosing the dominant minerals of the particular feature.

One such feature is the presence of relic algal structures, commonly outlined by disseminated iron oxides, that appear only in massive taconite-strata. Therefore, *algal (magnetite) quartz taconite* indicates the presence of these structures outlined by magnetite within a quartz taconite.

The presence of septaria structures, filled by quartz, within a quartzose massive taconite would be indicated by the rock name *septaria (quartz) quartz taconite.*

The presence of globular to irregular clusters of mineral grains within massive taconite-strata normally produces a mottled rock. Consequently, quartzose massive taconite containing porphyroblasts of a silicate is named a *mottled (silicate) quartz taconite.* Similarly, taconite containing remnants of unreplaced quartzose material in a silicate-rich groundmass is called *mottled (quartz) silicate taconite.*

Where granule structures are found, the granules commonly occur in random close-packing within the massive taconite-strata, thereby generally constituting about 60 to 70 percent of the rock volume. The finely disseminated magnetite found in these dominantly quartzose, subspheroidal structures commonly does not exceed 10 to 15 percent of the granule volume. In some places the granules are sufficiently rich such that magnetite can constitute from 20 to 50 percent of the total rock volume, in which case the name *granule (magnetite) quartz taconite* is justified. One particular stratigraphic unit of the formation locally contains abundant magnetite-rich granules that are segregated into laminated zones where the individual thin lamellae consist of closely-packed granules. This distinctive unit merits the name *bedded granule (magnetite) silicate taconite.*

Conglomeratic beds, of both intraformational and extraformational origin, have been simply grouped as "conglomerates" in the older classifications. The rock name conglomerate normally implies a clastic rock type, which is misleading with respect to the beds found in the iron formation. The conglomeratic features of either origin are simply small internal structures that have locally developed to a minor extent within taconite strata that are essentially chemical sediments. The conglomeratic fragments of a given bed rarely exceed 10 to 15 percent of the rock volume, with the exception of the basal layer of the formation. In the writer's classification, the conglomeratic beds of both origins are distinguished as minor types of taconite.

Numerous intraformational conglomerates have locally produced a pebbly fabric in many of the massive quartzose taconite-strata. If these pebbles, commonly magnetite-rich, constitute more than 20 percent of the rock volume, the name *pebble (magnetite) quartz taconite* has been found to be useful. The features of the pebbly fabric of these rocks, however, is often best treated in the descriptive text concerning the rock.

In a few places, the presence of extraformational clastic fragments within the massive taconite-strata requires special names. Thus the presence of detrital material, for example sand-size grains of quartz within silicate-rich

zones of iron formation, is denoted by a name such as *clastic sand* (*quartz*) *silicate taconite*. Similarly, *clastic pebble* (*quartz*) *silicate-quartz taconite* correctly described the basal few feet of the iron formation.

MINES EXPERIMENT STATION,
UNIVERSITY OF MINNESOTA,
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A COMPARATIVE STUDY OF MAJOR ORE DEPOSITS OF CENTRAL BOLIVIA. PART II

F. S. TURNEAURE

PART II

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MINERALOGY OF THE VEINS

Hypogene Ores

The mineralogy of the veins shows a notable contrast with that of the wall rock, yet there can be no doubt that wall-rock alteration and vein formation were episodes in an essentially continuous process. As many as 35 or 40 vein minerals have been recognized in each district, but many of these occur in small quantity and only 10 or 12 are abundant (Table 9).

The five districts under review exemplify the major ore types of the Bolivian Andes, the tin and the tin-silver ores. The deposits of each type exhibit many points of similarity in mineralogy, yet the mineralization is varied in detail and is best summarized by reviewing each district separately.

Llallagua.—The mineral sequence and complex textures of the Llallagua veins have been described in detail elsewhere (71). The initial stage in the formation of the veins was the deposition of crude crusts of quartz, followed by bismuthinite and cassiterite; many high-grade veins are composed almost entirely of these three minerals (Table 9). Wolframite also belongs to this early stage, its deposition closely following cassiterite. Tourmaline occurs here and there as microscopic needles in the vein quartz but is chiefly

TABLE 9. HYPOGENE VEIN MINERALS

CENTRAL ORE ZONE

	Sericite	Tourmaline	Topaz	Quartz	Fluorite	Kaolinite	Alunite	Apatite	Monazite	Siderite	Barite	Bismuthinite	Wolframite	Cassiterite	Franckeite	Teallite	Pyrrhotite	Pyrite	Marcasite	Arsenopyrite	Stannite	Sphalerite	Chalcopyrite	Galena	Tetrahedrite	Andorite	Zinkenite	Jamesonite	Boulangerite	Bournonite	Matildite	Ruby Silver	Stibnite
Llallagua	W	W		●				O	X	●		O	X	●	O		●	●	●	O	X	O	X	(X)	G	G		G	G				G
Morococala	W	W	W	W						●				●		X	●	●	●	X	X	O											
Huanuni	W	W		W	X			X		●				●	(X)	X	●	●	●	O	O	O	X										
Potosi-(A)	W	?		O			X					X	X	●				●		O	●	O	X	X	●	O	X	X		X	X	O	X
Potosi-(B)				O								X	X	●			X	●		O		X											
Oruro	W	(W)		O		X	X				X			●	X			●	(X)	X	O	X	X	X	O	O	O	X	O	X			

(X) = Rare;

● = Abundant; O = Common; X = Minor; W = Occurs chiefly in altered wall rock; G = Reported by Gordon (26).

Potosi veins divided into two main types: (A) Tin-silver veins,
(B) Tin veins - Utne group.

a product of rock alteration. Gordon (26, p. 295) lists apatite, which is locally abundant, and monazite among the early vein minerals.

The second stage of deposition is represented by pyrrhotite and probably by franckeite as well. In the central tin-bearing area, where hydrothermal activity reached a maximum, the pyrrhotite has been widely replaced by minerals of later age, especially by pyrite, marcasite and siderite. However, residual grains and rods of pyrrhotite are widespread in the ore, and distinctive patterns produced in the replacement of pyrrhotite offer additional testimony of its former abundance. The degree of pyrrhotite replacement is remarkable, and numerous veins of the central zone give evidence of attack throughout their known vertical extent. Considerable pyrrhotite remains in the marginal zone of low-grade ore. Franckeite is locally abundant and is a common microscopic constituent of the ore. It forms corroded plates, some of which are badly distorted, thin fibers, and plumose aggregates. It is probably an early mineral, but its precise age with respect to pyrrhotite is difficult to determine.

The next event in the formation of the veins was the wholesale replacement of pyrrhotite, probably accompanied by some replacement of franckeite. The new minerals were deposited in two overlapping stages: (a) arsenopyrite, sphalerite and stannite, and (b) marcasite, pyrite, minor arsenopyrite, and siderite. These correspond respectively to the third and fourth stages of vein growth.

In the replacement of pyrrhotite, the basal parting of that mineral exerted important control, and consequently many details of texture shown by the

later minerals have marked parallelism. Steplike grain boundaries, rows of pyrite grains, and angular inclusions of pyrrhotite may all show a uniform orientation and may thus outline original pyrrhotite grains up to several centimeters across. Complex pseudomorphs and other unusual patterns are common among the new mineral aggregates.

Minerals of the third stage are widely distributed but not abundant in the high-grade ore. Arsenopyrite forms interstitial aggregates between pyrrhotite plates and also replaces pyrrhotite. Stannite and sphalerite, which generally occur together, favor pyrrhotite grain boundaries and early mineral contacts; they clearly show the influence of the pyrrhotite structure.

The extensive alteration of pyrrhotite is expressed chiefly in the deposition of marcasite and pyrite, the most abundant minerals of the fourth stage (71, p. 49–57). These minerals exhibit a number of interesting textures, the most distinctive of which is the open network. Numerous replacement veinlets first developed in the pyrrhotite, and the subsequent removal of the pyrrhotite between the veinlets produced the open network. As seen under the microscope, the veinlets or webs are composed mostly of pyrite, but some consist of a complex aggregate of arsenopyrite, pyrite, lamellar marcasite and concentric marcasite. Additional textures produced by replacement of pyrrhotite include: (1) abundant lamellar marcasite associated with cubes and grains of pyrite, (2) granular to euhedral pyrite with scattered rods and patches of pyrrhotite, and (3) concentric, slightly anisotropic iron sulfide in botryoidal and globular masses.

Siderite is also a characteristic mineral of the fourth stage, formed as a by-product of the pyrrhotite alteration. It occupies the space between marcasite lamellae, surrounds grains of pyrite, and forms numerous veinlets cutting the other minerals. Siderite deposition continued into the next stage of vein formation, in which it is closely associated with late sphalerite.

Certain textures shown by pyrite and marcasite seem to be pseudomorphous after franckeite rather than pyrrhotite and suggest that some franckeite was replaced by the late mineral group. These textures, briefly described below, have been discussed and illustrated in a previous article (71, p. 38–45), but Ahlfeld (1; 4, p. 66) and Gordon (26, p. 296) have questioned their interpretation.

Aggregates of lamellar marcasite and pyrite faithfully reproduce the broken and twisted plates of franckeite; compact pyrite, which surrounds deeply corroded remnants of franckeite, exhibits a mosaic of elongated grains that is entirely foreign to the pyrite habit (71, Fig. 20, 21). Plumose aggregates of franckeite seemingly represent late cavity fillings, but close examination indicates that these aggregates are not typical crustifications. Instead, the plumose material appears to be continuous with franckeite plates that extend into the adjacent pyrite-marcasite areas (71, Fig. 23). The plumose franckeite thus represents the distorted remnants of original plates that protruded into the cavities.

The franckeite is largely confined to the central area where pyrrhotite is extremely scarce. Only two examples were noted in which the two minerals

were in direct contact. Age relationships are indefinite but the contacts are sharp, with no evidence of the increased porosity that is so typical of late-stage replacement of pyrrhotite. It is concluded that franckeite is of relatively early age, its deposition preceding the wholesale destruction of pyrrhotite. Siderite is unquestionably later than franckeite.

The fifth and last stage of vein formation was one of open filling rather than replacement. It was characterized by sphalerite, siderite, pyrite and rare chalcopyrite. These minerals appear as tiny veinlets and irregular coatings. Sphalerite occurs generally in botryoidal and globular masses, in places mixed with siderite. Differences in texture and color serve to distinguish the late sphalerite from that of early age. Moreover, stannite does not accompany the late sphalerite. Late pyrite coats the sphalerite and fills fractures in the concentric masses. Wavellite, an abundant mineral, forms remarkable crusts of late age. It may be of hypogene origin but is classed as a supergene mineral by Gordon (26, p. 337), who points to apatite as the source of the phosphorous.

The five principal stages in the formation of the Llallagua veins are summarized in Table 10, where the sequence can be compared with that of other districts.

Huanuni.—The tin deposits of Huanuni comprise narrow fracture fillings, fissure veins and breccia lodes. A crude banding is typical of many veins, and in the breccia lodes, the ore and gangue minerals occupy the space between rock fragments. The small size of the rock fragments is an indication

TABLE 10

SEQUENCE OF VEIN MINERALS

Stages:	1		2	3	4	5
Llallagua	q, (tm)	bm, cs, (wf), (ap)	frk, po, asp	sl, (st), (cp)	mc, (asp), py, sd	sd, sl, (py), wv(?)
Huanuni	q, tm, (ap), (fl)	cs	(tl), po, asp	sl, st, (cp)	py, mc, sd	sd
Morococala	q, tm, (tz)	cs	tl, po, (asp)	sl, (st)	py, (mc), sd	sd, sl, (py)
Potosi	q, py, cs, (asp), (wf), (bm)		st, (cp)	td, (sl), (mt), ad	fo, rs, (gl)	aln
Oruro	q, py, cs, (asp)		(sl), (cp), st	td, ad	fo, gl, frk	kn, dk, aln, (q), (mc)

Minor minerals shown thus (wf).

ad—andorite
aln—alunite
ap—apatite
asp—arsenopyrite
bm—bismuthinite
cp—chalcopyrite
cs—cassiterite
dk—dickite
fl—fluorite
fo—lead sulfosalts
frk—franckeite
gl—galena
kn—kaolinite

Mineral abbreviations as follows:

mc—marcasite
mt—matildite
po—pyrrhotite
py—pyrite
q—quartz
rs—ruby silver
sd—siderite
sl—sphalerite
st—stannite
td—tetrahedrite
tl—teallite
tm—tourmaline
tz—topaz
wf—wolframite
wv—wavellite

of considerable replacement of the fragments during ore deposition. The mineral sequence, as indicated by laboratory investigations (31, 72), is similar to that of Llallagua (Table 10).

Quartz and tourmaline, the dominant alteration products, occur locally as early vein minerals. Cassiterite was deposited next. It replaces the wall rock, corrodes the quartz and tourmaline, and fills space between quartz crystals. Fluorite and minor apatite are found with these early minerals.

The second stage in deposition is marked by abundant pyrrhotite, together with minor arsenopyrite and teallite. Pyrrhotite was extensively replaced by stannite, pyrite and marcasite, and these minerals show the typical textures inherited from pyrrhotite. Alteration, however, was not as complete as at Llallagua; many veins of the central zone still contain considerable pyrrhotite.

Arsenopyrite, which is common in some veins, was probably deposited somewhat later than pyrrhotite as it generally favors pyrrhotite grain boundaries and includes oriented patches of pyrrhotite. Teallite is relatively rare in the tin veins of the central zone, and in only two polished sections was it noted in contact with pyrrhotite. In these sections, plates and needles of teallite form a few clusters surrounded by pyrrhotite. A local parallelism of the small plates may reflect the pyrrhotite cleavage although generally the teallite forms radiating groups that bear no relation to the pyrrhotite structure. Specimens from the Maria Francisca mine, which lies beyond the pyrrhotite zone, show teallite, sphalerite and pyrite. The pyrite clearly replaces teallite, and odd, curved grains of sphalerite suggest that this mineral is also later than teallite. The teallite is not a late crustification, nor is it accompanied by siderite, which is generally associated with sulfides that have replaced pyrrhotite. Teallite is included as a mineral of the second stage; it may be slightly earlier or slightly later than pyrrhotite.

Next in the sequence of deposition are stannite and sphalerite, together with a little chalcopyrite. Stannite for the most part has replaced pyrrhotite, and the two minerals form compact aggregates. The stannite favors contacts with early cassiterite; many large grains and aggregates of cassiterite are separated from pyrrhotite by bands of stannite. This mode of occurrence suggests that stannite has formed by simple reaction between cassiterite and pyrrhotite, but there is no source of copper among the early vein minerals. Although migrating solutions thus contributed copper to the deposition of stannite, a large part of the tin was probably derived from the partial re-solution of cassiterite. Sphalerite occurs with stannite in a few specimens, the two forming compact mineral aggregates without a notable difference in age. Sphalerite is very common in the marginal veins of Maria Francisca whereas stannite is rare.

The principal minerals of the fourth stage are pyrite and marcasite, together with siderite. These minerals have been derived largely from the replacement of pyrrhotite, and the textures resemble those of Llallagua. Most of the pyrite has a smooth yellow surface, but some is finely pitted and has a gray color in polished section. The gray pyrite is commonly in concentric form and may be slightly anisotropic. Siderite and marcasite occur

with the pyrite, but the proportion of marcasite is much less than at Llallagua. Another variety of pyrite consists of aggregates of platelike units. These have highly serrated borders and are surrounded by siderite. Pyrite of this type has been derived from some platy mineral, but relict grains of pyrrhotite have not been observed in the pyrite plates. Many veins at the margin of the district contain pyrite, most of which may represent an original deposition rather than a replacement of pyrrhotite. The replacement of teallite by pyrite is recorded in specimens from the Maria Francisca dump.

The fifth and last stage in the development of the tin veins is represented by siderite. It was deposited in large part with pyrite and marcasite, but some siderite fills tiny fractures of distinctly later age (Table 10).

Morococala.—The tin ores of Morococala have not been described heretofore, but recent investigation by Hosmer (33) has brought out a number of interesting features. Quartz and tourmaline, the dominant minerals of the altered graywacke, do not appear in the typical vein; yet cassiterite, the first of the vein minerals, was deposited largely by replacement. This applies to the cassiterite of the narrow veins with their sharply defined walls, as well as to the less regular bands in which the texture of the graywacke is clearly reproduced by the fine-grained cassiterite aggregate.

During the second stage of vein growth, open filling prevailed, and the chief mineral to be deposited in the fractures was pyrrhotite. The pyrrhotite has been almost completely eliminated throughout the deposit, but the prevalence of microscopic inclusions in later minerals testifies to its former abundance. A little teallite was noted in a few polished sections. It is rarely in contact with pyrrhotite, but relationships shown between teallite and pyrite that was derived from pyrrhotite indicate that teallite was probably deposited before pyrrhotite (33, p. 22). Arsenopyrite, which occurs in minor quantity, is somewhat later than pyrrhotite.

Sphalerite, the next mineral of the sequence, is common in low-grade ore and is abundant in veins of the Reserva section (Fig. 16). It has formed partly by open filling but mostly by replacement of the wall rock. This combination has produced two contrasting patterns whose boundary marks the edge of the original open fracture. Clear sphalerite of the veinlet is bordered by altered graywacke, in which sphalerite has selectively replaced quartz, leaving residual grains and needles of tourmaline. Associated with the sphalerite is a little stannite of slightly later age.

Pyrite is extremely abundant, associated chiefly with marcasite and siderite. These minerals have developed by the replacement of pyrrhotite and exhibit the textures characteristic of this alteration. Some pyrite of granular form occurs in the wall rock beyond the pyrrhotite veinlets; this pyrite has selectively replaced the sphalerite of the altered graywacke.

The final stage in deposition is represented by crusts of siderite and sphalerite with a little pyrite. The late sphalerite has a botryoidal habit and the pyrite assumes concentric forms. A little quartz occurs as late gangue.

The mineral sequence at Morococala is comparable to that of other tin

districts (Table 10), but the ores are distinctive in that cassiterite, the first vein mineral, has formed largely by replacement of the wall rock.

Potosi.—The tin-silver ores of Potosi are distinguished by the great variety of ore minerals and by the abundance of pyrite rather than pyrrhotite among the early sulfides. Overlap in deposition is characteristic and repeated banding is noted in some veins. Lindgren and Creveling (45) and Jaskolski (34) have studied the ores in detail, and other investigators (2, 23, 49) have contributed additional notes on the mineralogy.

The earliest group of vein minerals is made up of quartz, pyrite, cassiterite, and arsenopyrite. Considerable pyrite was deposited before cassiterite, and definite overlap between the two is indicated by repeated banding in the ore. Wolframite and bismuthinite, which are found in the deeper veins, should be included with the early vein minerals, as well as rare pyrrhotite (Table 10).

The second stage of deposition is marked by stannite, together with lesser amounts of chalcopyrite. Again overlap is characteristic as stannite is in part contemporaneous with cassiterite. According to Jaskolski (34, p. 76), tetrahedrite is about contemporaneous with stannite, but other investigators conclude that tetrahedrite is somewhat later than stannite, initiating the third stage of vein formation. Associated with tetrahedrite is sphalerite, as well as some andorite and perhaps matildite.

The fourth stage of vein growth is represented by ruby silver, jamesonite and boulangerite, together with minor sphalerite and galena. Alunite is the last mineral to be deposited; it occurs as small veinlets and irregular masses that cut the sulfide veins.

The preceding account of the mineral sequence suggests combining the several stages into two main periods of deposition. The first is characterized chiefly by cassiterite and pyrite, to which may be added bismuthinite and wolframite of the deeper veins. The second period includes a greater variety of minerals, but the most significant are stannite, tetrahedrite, sphalerite and ruby silver. The two age groups correlate in a general way with the principal ore types, the tin and the tin-silver ores. The two groups, however, are not entirely distinct, as some cassiterite may occur in the tin-silver ore, and overlap is noted between cassiterite and stannite.

Oruro.—The complex tin-silver ores of Oruro have been studied by Lindgren and Abbott (44), Kozlowski and Jaskolski (40) and more recently by Chace (19). These authors emphasize two distinct periods of deposition, the first including the tin ores and the second, the more complex ores of silver. The two periods may be further subdivided into five episodes or stages of deposition which are comparable to those of Potosi (Table 10).

The first stage in vein formation constitutes the tin ore of the district, a heavy sulfide assemblage composed of minor quartz, abundant pyrite and cassiterite, together with a little arsenopyrite. Tourmaline is locally abundant and belongs to this early stage (2, p. 78). Most of the pyrite was probably deposited before cassiterite, but both pyrite and quartz deposition continued after the cassiterite period. The first veins to form, according to

Chace, were made up of the minerals of the first stage, and there was a pronounced structural break following their deposition. The minerals of later age include the common sulfides, sphalerite, pyrite and chalcopyrite, and a varied assortment of sulfosalts. These minerals form delicate crusts and fibrous aggregates, fill open fractures, and exhibit a complex series of replacements.

Sphalerite was the first mineral of the second stage of deposition, and it was closely followed by chalcopyrite. Stannite, the next in sequence, occurs mostly as residual grains; it has been replaced largely by zinkenite. For the most part stannite preceded tetrahedrite, but a slight overlap is indicated by crystals of stannite coating tetrahedrite.

Tetrahedrite and andorite, the principal silver minerals, mark the third stage of vein growth. They form replacement patterns and appear as individual crystals resting on other minerals. The lead sulfosalts are distinctly later than the silver minerals. Zinkenite, boulangerite and jamesonite, the principal minerals of the group, occur in compact intergrowths, as fine coatings and as hairlike crystals. They have also replaced early sulfides, especially sphalerite and stannite. Galena and franckeite replace stannite and zinkenite and also fill independent fractures. The late age of the franckeite at Oruro is noteworthy, as well as its association with galena.

The last hypogene minerals to be deposited were kaolinite, dickite and alunite. Quartz in small amount is scattered through the silver ore, and a little marcasite occurs with the late gangue.

The first period of vein formation (stage 1) accounts for the tin ore, in which cassiterite is the only ore mineral. The second main period (stages 2–4) accounts for the silver ore, the principal silver minerals being tetrahedrite and andorite (Table 10). The two main periods, separated by a period of structural adjustment, are not equally represented in all veins.

Summary.—The essential points regarding the vein mineralogy and mineral sequence are summarized in Table 10. The contrast between the tin ores and the tin-silver ores is readily apparent.

The tin ores, as represented by the deposits of Llallagua, Huanuni and Morococala, show a rather remarkable similarity in sequence of deposition. The principal stages are: (1) quartz, tourmaline and cassiterite, (2) teallite or franckeite, pyrrhotite and arsenopyrite, (3) sphalerite and stannite, (4) pyrite, marcasite and siderite, and (5) late coatings of siderite, pyrite and sphalerite. Bismuthinite and wolframite are associated with cassiterite ores at Llallagua and Potosi; apatite is common at Llallagua. Unusual textures and pseudomorphic patterns produced chiefly by alteration of pyrrhotite are typical of all three districts.

The tin-silver ores of Potosi and Oruro are more varied, yet they exhibit some similarity in mineral sequence. The stages are: (1) quartz, pyrite and cassiterite with pronounced overlap, (2) stannite and chalcopyrite, (3) tetrahedrite and andorite, (4) lead sulfosalts, minor galena and ruby silver, and (5) late gangue, chiefly alunite. Ruby silver is an important ore mineral at Potosi whereas andorite is more abundant at Oruro.

Ores of the Oxide Zone

A study of the oxidation of the ores is handicapped by the lack of precise information as to the nature of the ore shoots mined in the past. This is particularly true of the oxidized silver veins, as these were worked during the Colonial period.

Among the products of supergene alteration, the most noteworthy are the phosphates of Llallagua. Wavellite is the most abundant of the group; vauxite and two related species have not been found elsewhere. The phosphate minerals, which occur in remarkable crusts, have been described by Gordon (26), who attributes them to the supergene alteration of apatite. In the remarks that follow, attention is directed to the ore bodies of the oxide-zone.

Tin Ores.—The typical tin vein, composed of quartz, cassiterite and iron sulfides, yields on oxidation a porous mass of iron oxide, ranging in color from yellow to brown and bright red. Residual, unaltered cassiterite is generally visible in the oxide ore. Some of the highly pyritic veins of Llallagua have changed to a honeycombed body of limonite, with cavities up to a meter across. The wide breccia zones at Huanuni are highly permeable and most of the ore bodies are oxidized. In places, the percentage of limonite is far greater than that of the rock fragments, and this raises some question as to the precise origin of the breccia. The great stockwork orebody of Morococala has been oxidized throughout, and over broad areas, the dense silicified graywacke has been changed to a soft, bleached rock referred to locally as "panizo." The change is due to percolating supergene solutions, which have destroyed the cementing material of the graywacke. The distribution of the bleached graywacke is carefully noted by the miners, as the stockworks are rarely commercial in the unoxidized zone where the graywacke is extremely hard.

The limonite of the tin veins ranges from a loose, fine-grained aggregate to a porous but very hard material. No detailed study of the oxidized veins has been made, but thin-section studies show that jarosite as well as limonite is common in the oxide ore. Cassiterite undergoes no significant alteration, and in the most heavily oxidized ore of Llallagua, the cassiterite retains its normal sharp borders. Radiating fibrous cassiterite, which resembles wood tin, is found at Llallagua; it is clearly hypogene. Similar material is found at Oruro, and Chace (19, p. 456) considers it largely if not entirely hypogene.

Stannite is probably decomposed by acid sulfate solutions and secondary cassiterite would be a normal product of such a reaction. A white powdery material, said to be composed largely of tin dioxide, has been noted at Potosi, and this may owe its origin to the alteration of stannite. Teallite is relatively resistant, but at Carguaicollo (73), some teallite plates in the oxide zone are partly replaced by a mixture of anglesite and secondary cassiterite. The teallite of Huanuni and Morococala might alter in a similar fashion, but the mineral is scarce in both districts. No oxidation products derived from franckeite have been identified, but the destruction of the fibers and their replacement by fine-grained gangue may be in part an oxidation effect.

Zones of supergene cassiterite enrichment have not been recorded in the Bolivian region. On the contrary, many low-grade sulfide veins have been enriched within the oxide zone by the partial elimination of the more soluble metals and the relative concentration of cassiterite.

Tin-Silver Ores.—The typical oxidized tin-silver vein consists of a mixture of limonite and jarosite, thus resembling the tin veins of the oxide zone. In some ore shoots, grains of cassiterite can be recognized in the porous mass, but generally the cassiterite is finely distributed.

The oxidation of rich silver ores should yield typical silver minerals of the oxide zone. According to reports, cerargyrite and native silver were characteristic of the oxidized ores of Potosi and Oruro, but it is curious that no veins of high-grade, oxidized silver ore have been encountered in recent years. However, the extent of the old workings at Potosi and the ruins of old mills in the valley below the Cerro offer testimony of the great mining activity of the past. Under conditions which prevailed during the Colonial period, it is likely that low-grade ores were extensively mined and perhaps contributed most of the silver. High-grade ore shoots were probably encountered, but the true character of the "bonanzas" is largely a matter of speculation. Similar uncertainties exist with respect to the oxidized silver ores of Oruro (18, p. 112; 19, p. 453).

ORE DISTRIBUTION AND HYPOGENE ZONING

The tin and tin-silver ores generally occur in distinct shoots, most of them having a limited vertical range. Considered collectively, the ore shoots within a district define an ore-bearing interval whose elevation varies considerably from vein to vein. Vertical zoning, marked by a consistent change in mineralogy with depth, has not been clearly demonstrated in the tin deposits of central Bolivia, but some semblance of vertical zoning is noted in the tin-silver districts of Potosi and Oruro. Lateral zoning of the regional type, so well illustrated by the ore deposits of northern Bolivia (75, p. 614–616), is not evident in the mineralized belt of central Bolivia, but lateral zoning on a local scale is suggested by mineral distribution at Llallagua and Huanuni.

Ore Distribution

Ore Shoots.—The ore shoots of the districts described range from major ore bodies 600 m or more in length to small pockets of ore only a few meters in length. Numerous ore shoots on major veins have a stope length of 200 to 300 m. The stronger veins average a meter or so in width, but the veins of Morococala, although relatively persistent, rarely exceed 15 cm. Countless small veins and branches are productive in each district, and narrow seams only 3 or 4 cm in width may be mined provided they contain a high-grade filling.

The larger ore shoots can be described only in general terms as most of them were mined in the past when only fragmentary records were kept. The Contacto ore shoot at Llallagua extended for as much as 400 m laterally

and for 250 m vertically, and large sections of the vein assayed 25 percent tin or more. According to reports, the San Jose-San Fermin ore shoot had a maximum stope length of 700 m and in places the ore extended for 600 m vertically. It was undoubtedly one of the greatest shoots of tin ore ever discovered.

Several large ore shoots have been mined at Potosi and Oruro, but it is doubtful whether they compare in size with the major shoots of Llallagua. The Mendieta-Rica vein at Potosi has a length of 700 m on the upper mine levels, but in depth the mineralization passes into several veins of the Utne group. The Tajo Polo vein, developed for 600 m vertically, was very productive on the upper levels, but the deeper ore is highly pyritic with most of the tin occurring as stannite. Three or four of the Oruro veins have been traced for 500 m laterally and 400 m on the dip. The San Luis vein is rather unusual, having a short strike length and much greater vertical continuity. The Grande vein at Huanuni, although not extremely rich, ranks as one of the largest, and in places the vein is bordered by zones of mineralized breccia up to 30 m in width.

Numerous small veins and branches of the larger veins have provided most of the ore in recent years. The ore shoots on the branch veins generally connect with those on the major veins, but some branch veins weaken structurally near the junction and pass into zones of sheeting. A low-grade or barren section may then appear between the ore shoot of the branch vein and that of the main vein. Examples of this type are rather common at Llallagua and have also been noted at Oruro (19, p. 373).

The ore shoots generally have assay boundaries, with a gradual decrease in grade of ore when calculated to stoping width. In some places the change is mineralogical and the vein maintains its normal width beyond the ore limits; in others the change from ore to waste is largely structural. Narrow veins pinch out and the stronger lodes pass into a network of small stringers too widely spaced to be minable.

A large tonnage of ore mined in the past was obtained from extremely rich ore shoots, some of which extended vertically for 250 m or more. In general, the high-grade ore was surrounded by ore of lower grade, and the bonanza shoots comprised only a part of the ore-bearing section of the vein.

The ore shoots of individual veins, as viewed in cross-section, define an ore-bearing interval of variable height which extends from one vein group to the next. As a rule, the position of the ore-bearing section of one vein differs considerably from that of adjacent veins. In the Huanuni district, for example, the ore shoots of the several veins show a difference in elevation of 400 m ore more. A similar situation prevails at Llallagua, Potosi and Oruro, although differences in elevation are less pronounced. Accurate information as to upper and lower limits of ore on individual veins is rarely available, but an indication of the ore interval is obtained from the extent of vertical development on each vein. The record for Potosi, Llallagua and Huanuni is summarized on the accompanying chart (Fig. 21).

Controls in Deposition.—The strongest veins occur in competent formations that readily fracture, but relations are not sharply defined and important

ore shoots occur in various formations. At Llallagua the quartz porphyry intrusive is the locus of intense fracturing, yet the rich Contacto vein is enclosed almost entirely by sedimentary rocks. In the Potosi district, numerous veins are found in the competent, silicified porphyry, but some of the stronger veins extend downward into the Paleozoic formations without much change in character. Veins in the bedded volcanics on the west side of the stock are notably weak, but several veins in the bedded volcanics on the east

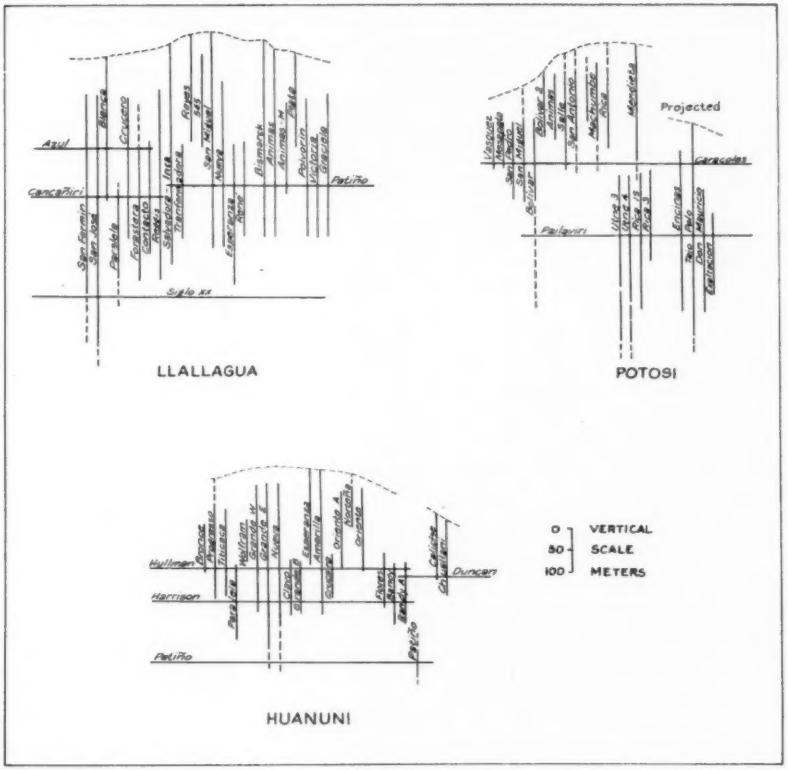

FIG. 21. Diagrammatic cross-section showing vertical development of major veins.

side have been very productive. The most persistent veins at Oruro occur in the quartz porphyry and San Jose breccia (19, p. 365). At Huanuni and Morococala, where igneous rocks are absent, the veins are most abundant in quartzite and in silicified shale or graywacke, rocks which are far more competent than the unaltered sedimentary rocks.

No consistent relationship has been found between the high-grade ore shoots and details of structure, such as vein dip, vein strike or vein width.

Nor can the position of the ore shoots be correlated with change in wall-rock type. As noted in subsequent paragraphs, the ore deposits were formed in a shallow zone close to the original surface. This environment would promote rapid changes in temperature and pressure, and such factors probably exerted greater control in ore distribution than local structure and nature of the wall rock.

Vertical Range in Ore.—The total vertical range in ore for each district, as indicated by development in 1949, is presented in Table 11. Also included is the interval of greatest production, within which the veins are more closely spaced and ore shoots are more abundant. Few tin deposits of Bolivia are productive below a depth of 650 m; they reach their maximum range in excess of 800 m at Potosi and Llallagua. Recent development of stockwork ore bodies on the Patiño level at Huanuni is noted by Ahlfeld (4, p. 49).

TABLE 11

VERTICAL RANGE IN ORE

District	Vein	Deepest level	Depth from surface	Interval of major production
Llallagua	San Jose	770	810 m	350 m
Huanuni	Small veins	Patiño	480	250
Morococala	San Francisco	211	230	150
Oruro	San Luis	480	600	300
Potosi	Utne Group	IX	875	350

Vertical Zoning

The appraisal of vertical zoning in ore deposits that have been worked for so many years is beset with difficulties. Many of the upper mine levels are no longer accessible, and reported mineral occurrences in abandoned mine areas are of doubtful value. Many veins have been thoroughly oxidized in their upper reaches and original differences in mineralogy have been destroyed. Successive stages in deposition add to the problem of interpretation, as early channelways may become effectively sealed during the later stages of mineralization.

In the Morococala district, mine development reaches a depth of only 250 m and is restricted mostly to the oxide zone. At Huanuni the hypogene ores show considerable variation from place to place but no systematic vertical change is indicated. At Llallagua, Potosi and Oruro there is a better opportunity to study vertical zoning, as the ores contain a greater variety of minerals and the veins are exposed over a greater vertical interval.

Llallagua.—The most notable feature of the Llallagua veins is the restricted vertical range of the high-grade cassiterite ore (26, p. 299; 71, p. 172). Many of the high-grade shoots pass upward into low-grade sulfide ore before the zone of oxidation is reached, but the sulfide filling of the upper levels seems to be the same as that exposed below the high-grade shoots. The deepest ore of the district is on the San Jose vein below the Siglo XX level.

This ore contains abundant arsenopyrite and considerable tourmaline, but both minerals are equally abundant elsewhere in the mine. The many low-grade, pyritic veins of the Siglo XX level are more representative of the deep ore than a single ore shoot. These veins resemble the low-grade veins at higher elevations, and there is no consistent variation of the sulfides with depth. The relationships described suggest that during the early stage of mineralization, conditions appropriate for cassiterite deposition were notably restricted, whereas during the later stages, more uniform conditions permitted the deposition of sulfides over a much greater vertical span.

Potosi.—The record suggests a vertical zoning of the tin and silver ores at Potosi, but mineral distribution is complicated by several stages in deposition, each characterized by a distinctive mineral assemblage. In the zone of oxidation, the principal veins were extensively mined for silver in the Colonial period, but numerous small veins have been worked for tin in recent years. The tin ore is generally low grade, but a few rich cassiterite shoots have been encountered.

Sulfide ores containing both tin and silver are characteristic of the Tajo Polo vein system, and most descriptions of sulfide ore refer to this section of the mine, where rather marked changes in mineralization with depth have been reported (2, p. 114; 23, p. 749; 45, p. 242). The silver ores, restricted to the higher levels, contain tetrahedrite, andorite and ruby silver. Ores rich in cassiterite have also been mined in the upper zone, but cassiterite gives way in depth to stannite, accompanied by chalcopyrite, bismuthinite and wolframite. Vertical zoning is thus expressed in silver above tin and cassiterite above stannite, and the record of production clearly indicates a marked decrease in silver with depth. Details of zoning, however, are masked by the variation in mineralogy of the several vein groups. The stannite ore of the Tajo Polo vein system, for example, is not fully representative of the deeper zone, as high-grade cassiterite ore is found at the same elevation in other veins, such as the Krause and Utnes (Fig. 14).

The several contrasting stages in mineralization are also critical in an interpretation of vertical zoning. Mineral distribution suggests that during the early stages, when most of the vein fractures were utilized by the ascending solutions, cassiterite was deposited throughout the ore zone, the high-grade tin ore being formed chiefly below the present zone of oxidation. During the later stannite-tetrahedrite stage, the Tajo Polo fracture system provided the main channelways. Tin-silver ores were then deposited, superimposed in many places on the early cassiterite mineralization. At this stage intensity differences were pronounced; stannite-rich ores prevailed in depth and ores rich in silver above. Some fractures, such as the Utnes, were scarcely mineralized during this period, and the original cassiterite ores were not modified by the later mineral assemblage. The final result is a certain zonal arrangement of minerals, but the pattern is complex and not the same in all veins.

Oruro.—Vertical zoning at Oruro is revealed principally in the relationship between the tin and silver ores (18, p. 113; 19, p. 452). In general,

the vertical range of cassiterite is less than that of the silver minerals, and the essential change with depth is from tin-silver to silver ore. Below a depth of 350 m the veins were mined mostly for silver, but in some of the stronger veins, tin persisted to a depth of 450 m or more. Local variations in the ore have also been noted. Some small veins at shallow depth were composed of pyrite and cassiterite without silver, and on the 350 m level, certain veins were unusually rich in silver whereas others contained the more complex tin-silver ore. Many of the differences in mineralogy can probably be explained by the varied permeability of the fracture systems during successive stages in mineralization. The early deposition of cassiterite was more restricted vertically and laterally than the subsequent deposition of the silver minerals (19, p. 453). In this respect the ores resemble those of Llallagua, where late sulfides are more widespread than early cassiterite.

Lateral Zoning

The most readily established outward change in mineralization is the reduction in the proportion of ore minerals and the increase in the common base-metal sulfides. Although the outlying veins exhibit a considerable range in mineralogy and comprise several types, the abundance of sulfides, especially sphalerite, suggests that they represent a lower intensity of deposition than do the tin and tin-silver veins of the central zone. Some veins of the outer zone contain small pockets of tin or silver ore, but there is no indication that at reasonable depth, the low-grade filling will pass into typical high-grade ore. Instead, the record suggests that the vague outer boundary of the central ore zone is relatively steep.

The Llallagua and Huanuni districts afford the best examples of lateral zoning, as the bed rock is exposed over a broad area and marginal deposits of several types have been found. Elsewhere some evidence of lateral zoning is noted in scattered underground workings, such as those of Reserva at Morococala, Tetilla at Oruro and Cerro Chico at Potosi (Table 12).

Llallagua.—The Llallagua tin-bearing zone, which covers an area of 1300 m by 1100 m, is partly surrounded by one in which several low-grade sulfide veins have been explored. The principal deposits are the Laguna, Callaperia and Patiño on the south side of the Salvadora intrusive and the Libertad and Estañina on the north side (Fig. 5).

Pyrite is the dominant filling in nearly all veins of the outer zone; sphalerite is widespread and is abundant in two prospects. Several small shoots of cassiterite ore have been encountered, as well as a few that show considerable silver. Accessory minerals include bismuthinite, arsenopyrite and stannite; franckeite was noted in one polished section. Pyrrhotite is widely distributed and has been replaced by pyrite, marcasite and siderite, these minerals forming textures similar to those developed in veins of the central zone. Some pyrite occurs as granular aggregates that give no evidence of an early platy mineral and some occurs as small grains and cubes replacing graywacke. This pyrite is probably an early mineral, about contemporaneous with pyrrhotite. Otherwise the sequence of deposition in the outer veins

TABLE 12

CHARACTERISTIC VEIN MINERALS OF THE CENTRAL AND OUTER ZONES

District	Vein zone	Quartz	Siderite	Bismuthinite	Wolframite	Cassiterite	Franckeite	Teallite	Cylindrite	Pyrrhotite	Pyrite	Marcasite	Arsenopyrite	Stannite	Sphalerite	Galena	Tetrahedrite	Andorite	Jamesonite etc.	Ruby Silver	Stibnite	Barite
Llallagua	Central Zone	●	●	○	x	●	○			●	●	●	○	x	○	(x)						
	Outer Zone	x	x	(x)		x	(x)			○	●	x	x	x	●							
Morococala	Central Zone	x	●			●		x		●	●	●	x	x	○							
	Reserva	x	x			○				○	●	○	x	x	●							
Huanuni	Central Zone	x	●			●		x		●	●	●	○	○	○							
	Maria Francisca	x				x	x	○	x	x	○	x	x		●	○			x		x	
	Quimsa Coya	●			●						x										○	
	Others	x				x					●				●							
Potosi	Central Zone	○		x	x	●				(x)	●		○	●	○	x	●	○	x	●	x	
	Cerro Chico	○									○		x		●	●			●			
	Others	x				x					●				●							
Oruro	Central Zone	○				●	x				●		x	○	x	x	○	○	●			
	Tetilla															●	○					○

● = Abundant; ○ = Common; x = Minor; (x) = Rare.

is substantially the same as that of the central zone. No subzones can be established on the basis of distinctive sulfides, and the principal outward change is a marked decrease in minerals of the early cassiterite stage.

Huanuni.—The central tin-bearing zone of Huanuni extends along the Huanuni anticline for 1,500 m and reaches a width of 1,200 m. To the south along the axis of the fold scattered veins and vein groups define an outer zone some 2.5 km in length. Most of the veins occur in the sandy formations, whereas very few veins have been found in the overlying black shale which occupies both limbs of the fold. The quartz porphyry dikes that occur along the eastern margin of the district are highly altered but are not ore bearing (Fig. 8).

Pyritic veins with sphalerite are most common in the outer zone. They usually contain very little cassiterite, but a small amount of ore has been produced from pyritic veins that crop out near the Patiño adit and along the Huanuni River to the southeast.

The Porvenir and Maria Francisca veins are characterized by zinc and tin with small pockets of silver ore (4, p. 50; 20, p. 486, 493). They have been developed by vertical shafts to depths of 200 m, but the workings have been under water for many years. Specimens from the Maria Francisca dump showed quartz, cassiterite, arsenopyrite, stannite, pyrite and abundant sphalerite. Teallite and a little franckeite were present but no cylindrite. The teallite is interstitial to early quartz and cassiterite and is replaced by pyrite and sphalerite. This sequence agrees with that observed by Davy

(20, p. 486), who noted that cylindrite and franckeite are later than quartz and cassiterite but earlier than stannite and pyrite. The specimens that he examined probably came from the Porvenir mine (67, p. 60–67). Additional vein minerals include jamesonite, boulangerite, wurtzite and siderite, as well as tetrahedrite and ruby silver. The Quimsa Coya vein, traced on the surface for 600 m, contains small shoots of tungsten ore (2, p. 88; 35). The vein filling consists of drusy quartz, hubnerite and stibnite.

The outer veins of Huanuni are more varied than those of the other districts. The pyrite-sphalerite and tin-zinc veins are clearly a part of the zonal pattern, but some question may arise as to the relation of the tungsten-antimony vein. However, pockets of wolframite have been found in the Huanuni mine and a little stibnite occurs at the Porvenir.

Other Districts.—Lateral zoning at Potosi is not well defined. Several cross-cuts that extend 200 to 300 m beyond the central zone have exposed low-grade veins containing more pyrite and sphalerite than the typical tin veins of the district. The small veins of Cerro Chico, 600 m north of the productive area, are rich in sphalerite, galena and boulangerite (34, p. 69). Accessory minerals are pyrite, arsenopyrite, chalcopyrite and stannite. The veins contain no cassiterite.

The Tetilla vein group at Oruro lies 700 m south of the central tin-silver zone. The veins in this area contain galena, tetrahedrite and barite but no tin minerals (19, p. 453). They were worked during the Colonial period for silver.

In the larger Morococala region, tin ores of high-temperature aspect are found at the Morococala, Santa Fe, Japo and Negro Pabellon mines (Fig. 7). These deposits, separated by as much as 6 km of essentially barren ground, probably represent distinct centers of high-temperature mineralization. At the Morococala mine itself there is some semblance of lateral zoning on a small scale. Veins of the outer zone, such as those of the Reserva section, contain much less cassiterite and more pyrite and sphalerite than do those of the main tin-bearing area (Fig. 16).

ORIGIN OF THE ORE DEPOSITS

As the ore deposits are associated with middle(?) Tertiary intrusions, it is appropriate to review igneous activity before considering the somewhat later episodes of rock alteration and ore deposition. Subsequent events, such as regional uplift, oxidation of the ore and late volcanism, are excluded from the discussion.

REVIEW OF IGNEOUS ACTIVITY

The flat-lying extrusive igneous rocks of the Potosi district mark the earliest period of Tertiary volcanism. The lowest volcanic formation extends 30 km west of Potosi, but the two overlying formations probably represent local accumulations of pyroclastic material, which was probably derived from volcanic vents in the Kari Kari Range, a few kilometers southeast of Potosi. Fine-bedded tuff of the uppermost member of the volcanic series

contains fossil plants of middle(?) Tertiary age, and as there is no indication of a major unconformity in the section, the volcanic sequence as a whole is assigned to the middle(?) Tertiary.

The quartz porphyry stock of Potosi cuts the uppermost volcanic formation, and the main intrusives of Oruro and Llallagua are believed to be of equivalent age. The intrusive bodies are all highly altered but of essentially similar character, ranging from dacite porphyry to quartz latite porphyry. The altered dikes of Huanuni and Morococala are also correlated with the Potosi stock.

The Salvadora intrusive at Llallagua probably represents a volcanic vent, and the San Jose stock of Oruro grades outward into bedded tuff of superficial character. These shallow-seated bodies of porphyry might be correlated with the earlier episode of volcanism that gave rise to the bedded volcanics of Potosi, but in structure, size, petrographic character and relationship to ore, the intrusives are more closely allied with the quartz porphyry stock of Potosi. It seems likely, therefore, that the bedded volcanics of Potosi are local in character and not represented in the other districts.

Cross-cutting bodies of breccia are common at Llallagua and Oruro, where they form dikes and lenses of steep dip. These occur chiefly within the intrusive rocks but some are completely enclosed by the older sedimentary formations. The breccia is composed of angular fragments of both sedimentary and igneous rocks, set in a finely fragmental matrix. The matrix may be in part a fine tuff, but it is not crystallized magma. The dikes are not intrusive bodies in the usual sense but are probably of explosive origin, closely related to the porphyry intrusions. As the breccia dikes are cut by the veins, their distribution gives a record of an early period of fracturing that closely followed intrusion but preceded the main period of mineralization. Some of the fractures occupied by breccia conform to regional trends, but others are highly irregular and owe their origin, perhaps, to local stress set up by the cooling of the intrusive igneous rocks. Small bodies of breccia similar to those of Llallagua and Oruro have been encountered at Morococala and Potosi. The Huanuni breccia, however, is composed exclusively of sedimentary material and is believed to be the product of hydrothermal leaching rather than explosive action.

HYPOGENE MINERALIZATION

Ore deposition in central Bolivia took place within a relatively shallow zone, probably within a few thousand feet of the surface. Supporting evidence is found in the geological setting of the deposits, vein structure, mineral assemblage, and ore texture. Many of the unusual features exhibited by the ores probably owe their origin to the combination of high temperature and low pressure, which is likely to prevail in the shallow zone, yet the broad sequence of events is more uniform than might be anticipated in ores of such diversity. The following main events may be recognized: (1) early stage of rock alteration, (2) intermineral fracturing and brecciation, and (3) principal ore stage with development of the veins (Table 13). That rock

TABLE 13. SUMMARY OF SEQUENCE OF EVENTS

	LLALLAGUA	HUANUNI	MOROCOCALA	POTOSI	ORURO
Intrusive activity	Salvadora vent Porphyry and porphyry breccia	Dikes east of mine area; weak intrusive power	Dike of mine area 2 - 5 m wide	Potosi stock cuts Cerro Rico volcanics of earlier age	San Jose and Itos stocks
Related volcanics	Volcanics eroded	Intrusive did not reach the surface	Intrusive did not reach the surface	Intrusive did not reach the surface	Tuffs & flows "grade into" intrusive
Early fracturing	Irregular fractures No pattern	Faulting along the Huanuni anticline	Zone of weakness along anticline	Intense fracturing upper part of stock	Irregular fractures
Explosive activity	Breccia dikes in part along fractures	- -	Possible breccia of Reserva section	- -	Breccia dikes along some fractures
Rock Alteration (Barren)	Early pervasive alteration of stock and breccia zones	Intense alteration NW trend	Intense alteration NW trend	Intense silicification upper stock; sericite below	Pervasive alteration of stocks; alteration of breccia zones
Principal fracturing	Vein system NE (NW). Veins cut dikes of altered breccia	Strong NE veins Vein clusters, fracture zones	Parallel NE veins Stockworks	NE Sheeted zone above; NE, ENE veins below	Strong veins, vein clusters, arcuate pattern
Period of leaching	Local breccia (?)	Drop in temp. and increased solution Corrosion breccia	Minor slumping of stockworks	Minor leaching, solution cavities in porphyry	- -
Formation of the veins	Tin ores	Tin ores	Tin ores	Tin-silver ores Tin ores (Utne veins)	Tin-silver ores
Late acid attack	Alteration of pyrrhotite - strong	Alteration of pyrrhotite - moderate	Alteration of pyrrhotite very strong	Alunite	Kaolinite, dickite, alunite (marcasite)
Late coating	Siderite,(pyrite), sphalerite. Wavellite (?)	Siderite	Siderite, sphalerite (pyrite)	- -	- -

alteration and vein growth were distinct but overlapping episodes is indicated by the field evidence and by the distribution of the altered rocks.

Wall-Rock Alteration

The general sequence of alteration is one of increasing intensity, ranging from mild chloritic alteration to sericitization and finally to intense silicification and tourmalinization. Chloritic alteration is widespread at Oruro, but in the center of the district, early chlorite was largely destroyed and abundant sericite was deposited. In other districts strong sericitization is typical of the porphyries.

Tourmalinization and silicification of the porphyry are believed to signify greater intensity of deposition than sericitization. In places, quartz and tourmaline are more abundant along permeable channelways where maximum temperatures would prevail, and both minerals replace sericite. Tourmaline and quartz are widespread in the altered porphyry at Llallagua and in the altered graywacke at Morococala. Tourmaline is less common than quartz at Huanuni. Silicification of the upper part of the Potosi stock is pervasive and unusually complete, yet the solution channelways cannot be identified. Feldspar phenocrysts were altered to an aggregate of quartz and sericite; the groundmass was converted to a fine quartz mosaic. The fact that phenocrysts generally are more susceptible to attack than groundmass suggests that early selective sericitization was followed by silicification. Alteration with increasing intensity may be postulated.

The stability field of the alteration products is not sufficiently limited to give precise figures as to the temperatures that prevailed during the alteration stage. Chlorite with subsidiary sericite is typical of the epithermal range,

which may be considered normal for the shallow volcanic environment. Lindgren (43, p. 454) places the temperature at 200°C or less, and Graton and Bowditch (29, p. 687) estimate the common range at 200–250° C. Sericite alone is not indicative as it may be deposited at widely varying temperatures, depending upon the nature of the solution. But the intensity of sericitization indicates that temperatures characteristic of the mesothermal range were built up in the most productive areas. Kerr (37, p. 331) gives a temperature of 250–450° C for the quartz epoch following the main sericite epoch of the porphyry copper deposits. Widespread tourmalinization points to unusually high temperatures for the shallow environment. Lindgren (43, p. 213, 637) lists tourmaline as characteristic of the hypothermal division, whose temperature range is estimated at 300–500° C. That alteration did not reach a uniformly high level in all districts is indicated by the fact that tourmaline is characteristic of the tin deposits but not of the tin-silver deposits.

Intermineral Fracturing and Brecciation

The distribution of the altered rocks provides the best evidence for an intermineral period of fracturing and brecciation. The altered graywacke at Morococala forms an oval area of northwest strike, which is transverse to the veins, and at Llallagua pronounced tourmalinization is controlled in part by breccia dikes and small fractures that are cut by the tin-bearing veins.

Early alteration in some areas evidently converted the original rocks into extremely brittle rocks that were readily fractured. The closely spaced veins of Morococala are largely confined to the altered graywacke; the sheeted zones of Potosi are limited to a brittle rock, the silicified porphyry; and the complex veins and breccias of Huanuni are found largely in silicified sedimentary rocks. The altered competent rocks would be particularly susceptible to tension failure, and many of the veins mentioned seem to be of the tension type. The stockworks, such as the Clavo Grande of Morococala, consist of highly broken rock; these likewise occur chiefly in areas of intense alteration.

The lenses of ore breccia at Huanuni are closely connected with the veins but are of uncertain origin. The breccia fragments are composed of altered sedimentary rocks similar to adjacent walls, but alteration is widespread and not restricted to the breccia zones. The breccia bodies show abrupt changes in strike and many veinlike branches; some grade downward into zones of highly fractured ground. This irregularity in outline and lack of continuity preclude a simple tectonic origin related to faulting (Fig. 20). The breccias might be of explosive origin, connected with igneous activity in depth, but there is little evidence of a throughgoing conduit. Moreover, the fragments are not of igneous character but consist of sedimentary rocks of local derivation. It is concluded that leaching by hydrothermal solutions offers the best explanation for the breccias. After intense fracturing of the silicified wall rock, hot solutions moved through the channelways and removed sufficient material to produce local slumping and brecciation. The main difficulty with the corrosion theory is the angularity of the fragments,

only a few of which are slightly rounded. Following brecciation, hydrothermal solutions introduced ore and gangue minerals to form ore bodies that are mineralogically similar to the veins. Local brecciation by solution action along fractures is noted in other districts and is well exemplified by the OK pipe of San Francisco, Utah (17, p. 516).

The ore-bearing breccias at Llallagua are more varied in character. They may owe their origin to hydrothermal leaching, but their location near the border of the porphyry suggests that they also had some connection with explosive activity of the Salvadora vent.

Formation of the Veins

Although rock alteration was well advanced before most of the vein fractures were formed, the two processes overlapped to some degree. A little cassiterite occurs with tourmaline in the altered porphyry at Llallagua, and disseminated cassiterite, likewise associated with tourmaline, is found in the altered graywacke of Morococala. In areas where early alteration had not produced a stable mineral aggregate, attack by solutions moving through the vein fractures continued, and narrow bands of altered rock were developed along many of the veins.

Stages in Vein Growth.—In the review of mineral sequence, five rather distinct stages of vein growth were outlined (Table 10). These may be summarized as follows:

(1) Cassiterite, the principal tin mineral in both the tin and tin-silver deposits, is the most characteristic mineral of the first stage. Quartz is conspicuous at Llallagua but subordinate elsewhere. Wolframite and bismuthinite are common associates of cassiterite; apatite, monazite, fluorite and tourmaline are less common vein minerals. In the mixed tin-silver ores of Potosi and Oruro, early pyrite is abundant, deposited in large part before cassiterite.

(2) During the second stage in deposition, cassiterite of the tin ores was followed by pyrrhotite, which was extensively replaced by sulfides during the two subsequent stages. Most of the arsenopyrite and probably teallite and franckeite belong to the second stage. In the tin-silver ores, the common iron sulfide is pyrite, an essential component of the first stage. The second stage in these ores is represented by stannite, minor chalcopyrite and perhaps sphalerite.

(3) The replacement of pyrrhotite of the tin ores was initiated during the third stage of vein growth with the deposition of stannite, sphalerite and minor chalcopyrite. In the tin-silver ores, the third stage is marked by the first appearance of the silver minerals, principally tetrahedrite with more or less andorite and possibly matildite.

(4) The general process of mineralization characteristic of the third stage continued into the fourth stage. Pyrrhotite that escaped early attack was widely replaced by aggregates of pyrite marcasite and siderite. Some tex-

tures suggest that these minerals also replaced teallite and franckeite. In the tin-silver ores, the deposition of sulfosalts continued. The minerals characteristic of the fourth stage are ruby silver, lead sulfosalts and, at Oruro, minor galena and franckeite.

(5) The fifth and last stage of mineralization is marked by coatings and mineral crusts. Siderite deposition persisted in the tin veins, accompanied by late sphalerite and minor pyrite. The final stage of deposition in the tin-silver veins is represented by late gangue, chiefly alunite or kaolinite.

Intensity of Deposition.—The mineral assemblage of the ore deposits gives evidence of deposition over a temperature range that is unusual for the shallow volcanic environment. Thus the early-stage vein minerals of the tin ores clearly belong to the hypothermal group: cassiterite, bismuthinite, wolframite and apatite. Tourmaline, which is uncommon as a vein mineral but abundant in the wall rock, is also typical of hypothermal deposits. In the tin-silver ores, cassiterite is the only early vein mineral of distinctly high-temperature aspect. Its association with pyrite rather than pyrrhotite suggests deposition near the lower limit of the hypothermal range. Thus the vein mineralogy, as well as the character of rock alteration, points to a lower maximum temperature in the tin-silver deposits than in the tin deposits.

The second-stage minerals of the tin ores are generally of lower intensity than those of the first. Although pyrrhotite is characteristic of many hypothermal deposits, its zonal position in the Cordillera Real (75, p. 615) indicates that it represents a lower temperature than the high-grade cassiterite ore. The significance of franckeite and teallite is difficult to appraise. Their occurrence in veins marginal to the central cassiterite zone, as at Huanuni, and in the highly distinctive tin-zinc deposits points to deposition in the middle temperature range; their replacement by pyrrhotite would imply a brief period of rising temperature. Minerals of the second and third stages in the tin-silver ores are not highly restricted in their occurrence. As pointed out by Chace (19, p. 463), however, minerals such as stannite, chalcopyrite and tetrahedrite comprise a typical mesothermal group and were probably deposited at higher temperature than the lead sulfosalts of the fourth stage.

Among the minerals of late age, marcasite is the most significant. According to experiments by Allen, Crenshaw and Merwin (5), marcasite is precipitated only from acid solutions but over a considerable range in temperature, deposition at high temperature requiring high acidity. The association of pyrite and marcasite with a carbonate, siderite, is evidence of low acidity and therefore of low temperature, perhaps no greater than 100–150° C. Alunite and kaolinite, late-stage minerals of the tin-silver ores, are likewise stable at low temperature, kaolinite being a common product of weathering.

The assemblage of vein minerals leaves little doubt that during the early stage of vein growth, particularly in the tin deposits, hypothermal intensities prevailed, with temperatures in the order of 400–500° C. Deposition continued with decreasing temperature, interrupted perhaps by minor reversals, and the last minerals to form were deposited at distinctly low temperature, perhaps in the range of 100–150° C.

Chemical Composition of the Ore Solutions

The nature of wall-rock alteration and mineralogy of the veins gives some clue as to the chemical character of the mineralizing solutions. The evidence, however, is not fully conclusive as detailed studies of the altered rocks have not been made and a difference of opinion exists as to the significance of the principal minerals.

Alteration Stage.—As an essential constituent of propylitized andesite, chlorite is a widely distributed hydrothermal product. It also occurs in the fringe zone of many areas of intense alteration, where it represents the initial, feeble attack by the mineralizing solutions. The distribution of chlorite in the mining districts of central Bolivia conforms with its marginal occurrence elsewhere. According to the prevailing view, chlorite is deposited under alkaline conditions at relatively low temperature.

Both Lindgren (43, p. 457) and Graton (28) emphasize the alkaline character of the ore fluid and point to the widespread development of sericite as evidence of alkali attack. Schmedeman (65, p. 803), Lovering and Tweto (48, p. 63–67), Burbank (14, p. 81), and Kerr (37, p. 330) agree that sericite is usually indicative of neutral to slightly alkaline solutions. The mineral, however, is not exclusively a product of such solutions as Gruner (30) has synthesized sericite in acid solutions at temperatures above 340–360° C. In the Butte district, sericite has been deposited in a chemical environment in which kaolinite was relatively stable and carbonates were not completely destroyed. Sales and Meyer (61, p. 27; 63, p. 272) conclude that the solutions were slightly acid, and pointing to the experiments of Gruner, they place the temperature somewhat below 340° C. That sericite may form from acid solutions is emphasized by Lovering (47, p. 249).

Sericite is a common and characteristic alteration product of the igneous rocks of the Bolivian districts, although locally quartz or tourmaline is more abundant. Minerals that are indicative of acid attack, such as kaolinite and alunite, are notably scarce or absent as alteration products, and the intensity of sericitization in some areas gives evidence of marked addition of potash by the mineralizing solutions. In view of these facts and general occurrence of sericite, the mineral may be logically attributed to slightly alkaline solutions at moderately high temperature. The mineral has been synthesized in alkaline solutions at temperatures of 225–300° C (57).

Silica may be transported by either acid or alkaline solutions and deposition of silica may take place from such solutions with reduction in temperature or by neutralization (46, p. 56). Strongly acid solutions commonly remove most of the bases but a large part of the silica and alumina combine to form the typical clay minerals. Some of the silica released from silicates may remain as quartz, or it may contribute to the formation of siliceous cappings above zones of argillic alteration (60, p. 185; 46, p. 48).

Widespread and almost complete silicification of andesitic lavas has taken place in the Bonanza district, Colorado. The feldspar phenocrysts have been replaced by kaolinite and sericite, and the groundmass has been converted to a fine quartz mosaic. Burbank (14, p. 81) compares this alteration to

changes observed in the vicinity of hot springs in volcanic regions, and he believes that acid sulfate solutions best account for the intense silicification. Such solutions are capable of strong leaching, and in places, the feldspar phenocrysts have been removed. Deposition of sulfides took place after silicification and was coincident with late sericitic alteration under alkaline conditions.

At Cerro de Pasco, Peru, the reverse sequence has been recorded by Graton and Bowditch (29, p. 679). Sericitization of the porphyry by alkaline solutions was followed by acid attack, as indicated by late deposition of quartz, alunite and kaolinite.

In the Red Mountain district, Colorado, described by Burbank (15, p. 161–205), the igneous rocks along the main channelways were strongly leached and the less soluble material was deposited nearby to form siliceous casings composed mostly of quartz and minerals of the kaolin group. In depth, silicification gives way to sericitization and the rocks are much more compact. The ore minerals, closely associated with sericite, were deposited within a restricted vertical interval, mostly in open space provided by earlier leaching. Acid attack continued, however, after the main ore stage; clay minerals locally vein the sulfides and the sulfides show effects of corrosion by late hypogene solutions.

To explain the close association of the two contrasting types of alteration, Burbank (15, p. 202; 16, p. 309) advances the theory that ascending sulfide-bearing liquids of alkaline type were vaporized, and at higher levels the vapors condensed to form an acid liquid that strongly attacked the rocks. The theory may well apply to ore deposits of the shallow environment, where solutions at high temperature may be subject to rapid drop in pressure with consequent local boiling.

Intense silicification is not restricted to the shallow volcanic environment but is recorded in a great variety of ore deposits. The replacement of limestone to form jasperoid, for example, is not uncommon, and quartz-sericite alteration is characteristic of the porphyry copper deposits. The jasperoid of the Tintic district is attributed by Lovering (46, p. 57) to nearly neutral bicarbonate solutions; the quartz and sericite of the altered porphyries, according to Peterson *et al.* (58, p. 840) and Kerr (37, p. 329), were probably deposited by alkaline solutions.

The silicified porphyry at Potosi closely resembles the altered andesite of the Bonanza district. A change from alkaline liquid to acid vapor by boiling of the solution at an appropriate level might also explain the contrast between the silicified porphyry of the upper levels and the sericitized porphyry at greater depth. The alteration, however, differs in several respects from the Red Mountain example described by Burbank. Silicification of the Potosi porphyry has produced a brittle rock, not marked by enlarged openings but by small cavities. Quartz has been introduced in large volume; it is not a residual product associated with clay minerals. Moreover, no indication has been found in depth of a zone of strong leaching that might correlate with the siliceous rock above.

The formation of the Huanuni breccia by corrosion involves deposition of silica followed by strong leaching of silica. Laboratory experiments conducted by Kennedy (36) on the solubility of silica in water may offer an explanation for this reversal in process. Within the high-temperature range, a drop in pressure with consequent expansion of the fluid results in pronounced decrease in the solubility of silica. After low pressure is attained, a reduction in temperature increases the solubility of silica. In the Huanuni district, for example, the fracturing of overlying formations might bring about a sudden release in pressure. This would correspond to the period of widespread silicification, when the solutions were saturated with silica but were capable of removing other constituents during replacement. After pressure release, a drop in temperature from say 450° to 350° C would promote the solution of silica, and corrosion breccias might be formed at favored localities. The postulated temperature range is compatible with the general nature of the mineralization.

It is evident from the examples mentioned that intense silicification may be the result of either alkaline or acid solutions, but minerals particularly suggestive of acid attack are not characteristic of the Bolivian districts. It is concluded, therefore, that silicification was effected for the most part at relatively high temperature and by neutral to weakly alkaline solutions.

Tourmaline, as a product of thermal metamorphism of argillaceous sediments, may be deposited by fluids that escape from the magma during an early stage in crystallization. Such fluids, according to Bowen (11, p. 118–119) and Fenner (24, p. 78), consist of gases of strong acid reaction. Tourmaline occurs with cassiterite in many tin deposits. The experiments of Daubree, in which he synthesized cassiterite by reaction between $SnCl_4$ and water, and the fluorine content of tourmaline have led to the theory that both minerals are formed by acid vapors containing the halogens. The theory, however, is rarely applied to the tungsten minerals, which are so commonly associated with cassiterite.

Tourmaline may also be deposited in an alkaline environment. It is recorded as an original constituent of granite and aplite (66, p. 163), and it appears as an accessory mineral in pegmatites, grouped with minerals of the magmatic stage (42, p. 97). The occurrence of tourmaline veins well within the intrusive bodies suggests that the mineral is deposited by residual fluids of late derivation. Shand (66, p. 166) believes that both tourmaline and cassiterite are formed by such fluids and sees no reason to assume that the transporting agent was gaseous rather than liquid. Bowen (11, p. 118), Graton (28, p. 327) and others agree that magmatic fluids of residual origin are liquids of alkaline character. On the basis of laboratory experiments, Smith (69) concludes that tourmaline is deposited exclusively from alkaline solutions.

The widespread development of tourmaline in the Bolivian province is noteworthy. In the Llallagua district, tourmaline is typical of the altered porphyry where it is associated with sericite and quartz rather than with cassiterite. As indicated previously, sericite was probably deposited from

slightly alkaline solutions, and the tourmaline can be attributed to the same solutions. Tourmaline also occurs with quartz and a little sericite in the altered sedimentary rocks of Huanuni and Morococala. This mineral assemblage largely reflects the composition of the original sedimentary rocks, but fluorine and boron have been added, possibly by a process akin to thermal metamorphism. There are, however, no indications of intrusive bodies comparable in size with the altered zones and no evidence of acid attack. It is concluded, therefore, that the alteration was produced by residual hydrothermal solutions similar to those that attacked the porphyry in other districts. Theories based upon the combination of tourmaline and cassiterite carry little weight, as the two minerals are not intimately associated in the Bolivian districts.

Main Period of Vein Growth.—The most important early vein mineral is cassiterite, associated in the tin deposits with quartz, bismuthinite, wolframite and apatite. These minerals are found in many high-temperature deposits of the deep vein-zone and of near-source position and were probably deposited by alkaline solutions. Tourmaline is also characteristic of the deposits but it occurs in the altered wall rock and rarely as a vein mineral with cassiterite. As emphasized previously, there is little reason to classify these minerals as of pneumatolytic origin, to be distinguished from others of high-temperature character. Smith (68) has pointed out that cassiterite may be deposited from alkaline sulfide solutions as well as from acid vapors, basing his conclusions on laboratory experiments. It is noteworthy that cassiterite in the tin ores is followed by pyrrhotite, which seems to be highly unstable in an acid environment. The early-stage minerals of the tin-silver deposits likewise suggest alkaline conditions. Cassiterite is associated chiefly with pyrite in these deposits, and tourmaline is absent except within a restricted area at Oruro.

Hypogene mineral zoning is a notable feature of the Bolivian deposits, expressed chiefly in the limited vertical range of the high-grade ore. Hydrothermal solutions reaching a shallow zone while still at high temperature would be subject to marked changes in temperature and pressure. A sudden release in pressure coincident with a period of fracturing or brought about by the movement of solutions into a highly fractured zone might induce local boiling. This would greatly accentuate the normal tendency for rapid precipitation in the shallow zone. Such an episode of pressure release has been suggested to account for the shallow but high-grade cassiterite shoots of Llallagua (71, p. 178). But deposition probably did not take place in a strongly acid solution as there is no evidence of argillic alteration nor of pronounced acid leaching contemporaneous with cassiterite deposition. Pyrrhotite and other minerals of the next stage extend vertically throughout the deposit and were probably formed at lower temperature. Their deposition may correlate with a period when pressure was more uniform and liquid solutions again moved through the channelways. Chace (19, p. 469) likewise favors local boiling of the ore solution as a factor in vein growth, but he places this episode relatively late in the depositional history of the veins.

It should be noted that emphasis is placed not on major transport of metals in the vapor phase but on the generation of a gas as a factor in promoting mineral deposition.

Another factor that may be important in determining the assemblage of ore minerals is the concentration of sulfur in the ore solution. The effect of concentration is difficult to appraise but under some conditions it seems to be a critical factor. In their study of the Butte veins, Sales and Meyer (62) conclude that sulfur concentration has had an important effect; low concentration promotes deposition of chalcopyrite and bornite and high concentration favors pyrite and chalcocite. In a recent article, McKinstry and Kennedy (52) examine the possible role of sulfur in the sequence of mineral deposition. They point out that in the copper-iron-sulfur system the chemical potential of sulfur probably increases during ore deposition and that late mineral assemblages are enriched more and more in sulfur.

No direct parallel can be drawn between the mineral sequence disclosed in the Bolivian ores and the examples mentioned, but sulfur concentration may provide the key to relationships shown by cassiterite and the two iron sulfides, pyrite and pyrrhotite. In the tin ores, cassiterite consistently precedes pyrrhotite, and there is little evidence of overlap between the two. In the tin-silver ores, the iron sulfide is pyrite rather than pyrrhotite, and there is a decided overlap with most of the cassiterite following pyrite. In the solutions that formed the rich cassiterite ore the sulfur content may have been unusually low; this would lead to the deposition of pyrrhotite rather than pyrite and might also explain the early age of the cassiterite. In the solutions that produced the tin-silver ore, the sulfur concentration may have been much higher; this would favor pyrite rather than pyrrhotite and conditions causing deposition of pyrite might also delay the precipitation of cassiterite.

The franckeite at Llallagua seems to belong to an early stage, whereas tin sulfosalts would be expected to form at a late stage, along with other soft platy minerals. Ore solutions having an unusual concentration of tin combined with low sulfur may account for the early deposition of franckeite. Bismuthinite, which is also a soft platy mineral, affords another exception to the rule that soft minerals are generally late, as it is essentially contemporaneous with cassiterite and earlier than pyrrhotite.

Following the deposition of cassiterite and the iron sulfides, tin and iron continued to be precipitated but they combined with copper to form stannite, generally accompanied by minor chalcopyrite. These minerals, widely distributed, are of about the same age as sphalerite. Tetrahedrite and andorite were deposited next in the tin-silver ores, followed shortly by lead sulfosalts and ruby silver. That conditions appropriate for deposition of franckeite may develop at a late stage is indicated by the cross-cutting veinlets of franckeite and galena at Oruro.

The manner of transport of the metals remains a major problem. The common sulfides are soluble in acid solutions and some have been synthesized in alkaline sulfide solutions. Most ore deposits give little evidence of strong

acid attack during the main ore stage, and it seems likely that the common sulfides and sulfosalts were deposited under neutral to alkaline conditions. The main feature of the Bolivian ores that may be significant from the standpoint of sulfide deposition is the widespread destruction of pyrrhotite during a late stage of hypogene deposition. This change may mark a shift from alkaline to acid conditions.

Late Acid Attack.—The best evidence of late-stage deposition by acid solutions is provided by the tin ores. It involves the conversion of pyrrhotite into an aggregate of marcasite, pyrite, and siderite. The change from pyrrhotite to pyrite, as pointed out by McKinstry and Kennedy (52, p. 387–389), may be brought about in several ways: by increase in concentration of sulfur under constant temperature, by decline in temperature while sulfur concentration remains constant, or by decline in both variables. However, the replacement of pyrrhotite in the Bolivian ores is so nearly complete in many veins that a more pronounced change in physico-chemical conditions is implied. The replacement of pyrrhotite by pyrite is recorded in many districts, whereas the replacement by pyrite, marcasite and siderite is relatively rare. This combination might be accounted for by a drop in temperature or by an increase in sulfur concentration, but it is believed that solutions of acid character played a dominant part in the late alteration of pyrrhotite.

According to experimental evidence (5), marcasite is deposited only from acid solutions. The presence of siderite with the marcasite and pyrite indicates that the solutions were neither strongly acid nor at high temperature, but their precise nature is difficult to determine. The change from pyrrhotite to pyrite and marcasite requires removal of iron or addition of sulfur, but as a rule, the mineral aggregate is vuggy rather than compact. This suggests that the chemical balance may have been attained in part by the removal and re-distribution of iron. The prompt deposition of a large amount of iron as carbonate indicates that the solutions were rich in dissolved carbon dioxide; the deposition of late pyrite in part mixed with siderite points to the presence of appreciable sulfur. The occurrence of late pyrite and sphalerite as crusts and botryoidal coatings may signify a change from acid to neutral or slightly alkaline solutions during the final episode of vein growth.

The record of late acid attack is less striking in the tin-silver ores than in the tin ores. It consists chiefly in the presence of late kaolinite, dickite and alunite. Chace (19, p. 467, 469) believes that the solutions were distinctly acid in reaction when these minerals were deposited, and he suggests that local boiling of the solutions may have taken place with the development of an acid gas.

Several theories have been proposed to account for the late generation of an acid sulfate solution from an alkaline sulfide solution. The formation of acid by reaction with ferric iron compounds does not seem to apply to the Bolivian districts as the rocks are low in ferric minerals, and the changes took place well below the exposed ore bodies at depths that would probably rule out the influence of atmospheric oxygen. A third method of acid gen-

eration has been advocated by Graton (27, p. 541) and has been applied specifically to the ore deposits of Cerro de Pasco by Graton and Bowditch (29, p. 683–691). It involves a reaction between water and sulfur compounds in the solution, resulting in the formation of sulfuric acid and hydrogen sulfide. The reaction, according to Graton, is favored by the combination of low pressure and high temperature. This special condition would likely develop in the near-surface zone if high temperature is maintained by preheating of the channelways or if fracturing brings about a sudden release in pressure. Moreover, if conditions are extreme, boiling of the solution may occur and the resulting gas would be of acid character (28, p. 348–349).

The late generation of acid by the method described is correlated with a late period of vein reopening at Cerro de Pasco (29, p. 690); the same explanation is favored to account for late acid attack at Oruro (19, p. 468) and at Llallagua (71, p. 184). The presence of alunite at both Cerro de Pasco and Oruro points to acid solutions of the sulfate type, whereas the abundance of siderite at Llallagua points to solutions rich in carbon dioxide. Simple boiling of an alkaline solution at an appropriate, shallow level, as noted by Burbank (15, p. 193–202), will yield an acid gas, which on condensation might produce the observed modification of the sulfide ore.

SUMMARY: SEQUENCE OF EVENTS

The ore deposits of central Bolivia are closely related to the volcanics and quartz porphyry intrusions of middle(?) Tertiary age; all probably owe their origin to the differentiation of the same parent magmas in depth. The flows and bedded tuffs of Potosi represent the earliest episodes of volcanism, whereas the porphyry intrusions, as well as the explosive vent at Llallagua, are somewhat later manifestations of igneous activity (Table 13).

The intrusive igneous rocks of the region are of shallow-seated character, and the ore deposits likewise were formed relatively close to the original surface. The nature of rock alteration and the vein mineralogy give evidence of deposition at temperatures well above those that normally prevail in the near-surface zone. Although the intrusion of magma introduced some heat into the shallow zone, the ore solutions themselves provided the principal heat source. As the solutions continued to flow, the temperature along the channelways gradually increased. This period of rising temperature is correlated with rock alteration and the progressive development of chlorite, sericite, quartz and tourmaline (Table 13). The concept of advancing alteration fronts, which Sales and Meyer (61) have applied to the alteration zones at Butte, is consistent with the alteration pattern in the Bolivian districts, although the vein fractures did not provide the main channelways during this period of mineralization. Instead, the solutions were guided in part by breccia dikes, contacts and irregular fractures; in places, alteration was so intense and pervasive that the early channelways have been completely obliterated.

After rock alteration was well advanced, extensive fracturing took place and vein growth was initiated. Maximum temperatures were probably reached during the late stage of rock alteration and early stage of vein growth, when cassiterite was being deposited in abundance. During subsequent growth of the veins, deposition of sulfides and sulfosalts probably took place on a decreasing temperature scale. That the maximum temperature reached in the tin-silver deposits was somewhat less than that of the tin deposits is suggested by the contrast in mineralogy of the two ore types.

The mineralogy of the veins differs markedly from that of the altered wall rock. The reason for this contrast is a matter of speculation but may reflect a fundamental change in the solutions at the source, those of later derivation being relatively rich in metals. This theory, stressed by Neumann (55) and Lovering (46, p. 62), seems to offer the best explanation for the observed relationship.

Both the tin and tin-silver ores combine minerals characteristic of the high-intensity and low-intensity groups; temperatures probably ranged from 400° or 500° C when tourmaline and cassiterite were being deposited to a low of 100–150° C during the pyrite-marcasite-siderite stage. Rapid changes in temperature and pressure, which are likely to take place in the shallow zone, are reflected in high-grade ore shoots, in unusual mineral assemblages, and in complex ore textures. A release in pressure combined with drop in temperature might explain the formation of corrosion breccia, which involves a shift in solution chemistry from silica deposition to silica leaching.

A rapid reduction in pressure would also promote the generation of a gas phase if the solutions were at high temperature. The liquid and vapor phases would be of contrasting character, and the boiling of an alkaline liquid might yield a gas of acid reaction. However, the mineralogy suggests that solutions of neutral to weakly alkaline character prevailed during the period of alteration and early vein growth. More convincing evidence of acid attack is found in the late alteration of pyrrhotite and in the deposition of alunite and kaolinite. Perhaps local boiling contributed to the formation of acid fluids during the late stages of mineralization, but the combination of high temperature and low pressure might promote reactions within an alkaline fluid that would yield an acid fluid of the sulfate type.

In conclusion, it may be noted that the five ore deposits described, although varied in structure and mineralogy, were all formed in the shallow zone and all possess the characteristics of the xenothermal class as defined by Buddington (13). The degree of telescoping is perhaps greater at Llallagua and Huanuni than at Oruro and Potosi. Morococala might be designated as a hypothermal tourmaline-cassiterite-pyrite deposit, but microscopic study reveals the complex depositional history of the ore and its resemblance to the telescoped, xenothermal tin ores of Llallagua and Huanuni.

UNIVERSITY OF MICHIGAN,
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SCIENTIFIC COMMUNICATION

THE GEOCHEMISTRY OF RHENIUM—ADDENDUM

MICHAEL FLEISCHER[1]

WHILE my review (2) of this subject was in press, two papers appeared in the U.S.S.R. to which attention should be called.

The first of these, by Zhirov and Ivanova (4), gives 19 new determinations of rhenium in molybdenites and also quotes some additional data by Basitova (1), not previously available in the United States. These analyses, made by a colorimetric method, are summarized in Table 1. From them, Zhirov and Ivanova draw the conclusion, stated by them to have been reached previously by Basitova (1), that the content of rhenium in molybdenites increases as one goes from high-temperature to medium-temperature deposits.

TABLE 1

RHENIUM IN MOLYBDENITES FROM DEPOSITS OF VARIOUS GENETIC TYPES
(MODIFIED FROM ZHIROV AND IVANOVA, 1959)

Type of deposit	Name of deposit	No. samples	Range of content Re ppm	Av. content Re ppm	Ref.
Skarn	Tyrny-Auz, northern Caucasus	—	—	3.2	(1)
Cassiterite-wolframite-molybdenite (high-temperature)	*Central Kazakhstan*				
	Kara Oba	12	1.0–5.8	3.3	(4)
	Akchatau	1	—	1.2	(4)
	Airshoko	1	—	2.7	(4)
	Dal'nensk	1	—	2.2	(4)
Molybdenite-pyrite (transitional from high-temperature to medium-temperature)	Shalgiya, Central Kazakhstan	4	22–39	32	(4)
Molybdenite-chalcopyrite (copper-molybdenum, medium-temperature)	Kounrad, Central Kazakhstan	—	—	150	(1)
	Kajaran, Armenia	—	160–410		(1)
	Aigedzor, Armenia	—	—	780	(1)

The data are interesting; the large variations among the molybdenites of porphyry copper deposits remain unexplained.

The second paper, by Satpaeva, Kalinin, and Fain (3), described a rapid, but sensitive spectrographic method that permitted study of many concentrates and ores from the Dzhezkazgan deposits of Kazakhstan. Their data on the

[1] Publication authorized by the Director, U. S. Geological Survey.

ores are given in Table 2. The results are surprising in that rhenium is found in appreciable amounts not only in copper-rich but also in lead-rich and zinc-rich ores, and apparently is present in some mineral other than molybdenite, although the rhenium and molybdenum contents are stated to be similarly distributed. Further study of the mode of occurrence is evidently necessary. The highest content of rhenium noted is in a concentrate of bornite ore containing Cu 56.3%, Re 150 ppm.

TABLE 2

RHENIUM AND MOLYBDENUM IN ORES OF DZHEZKAZAGAN, KAZAKHSTAN (AFTER SATPAEVA, KALININ, AND FINE (3))

Type of ore	Re			Mo		
	No. samples analyzed	No. positive results	Content in ppm	No. samples analyzed	No. positive results	Content in ppm
Sulfide ores of first phase of mineralization						
Chalcopyritic ore	24	22	trace to 40	13	11	trace to 30
Bornitic ore	60	57	trace to 50	44	43	trace to 50
Bornite-chalcopyrite ore	32	29	1 to 40	13	12	<3 to 50
Chalcocitic ore	20	17	trace to 40	15	15	trace to 50
Galenitic ore	13	13	3 to 40	6	6	<10 to 50
Sphaleritic ore	10	8	1 to 30	7	6	<10 to 50
Minerals of the second phase of mineralization						
Chalcopyrite	8	—	—	7	3	trace
Bornite	9	2	trace	7	2	trace
Chalcocite	5	2	trace	3	1	trace
Sphalerite	4	—	—	3	—	—
Pyrite	1	—	—	1	1	trace
Galena	3	—	—	3	1	trace
Tetrahedrite	7	—	—	4	—	—
Domeykite	1	—	—	1	—	—
Mixed (sulfidic-oxidized) and oxidized ores						
Chalcocitic ores	5	4	trace to 7	—	—	—
Mixed ores	42	25	trace to 10	40	31	trace to 30
Oxidized ores	47	8	<1	26	14	trace to 40

The paper also presents data on samples from the Dzhezkazgan beneficiating mill and the Karsakpaisk copper smelter; these are given in Table 3.

The data in this paper confirm the possibility previously stated (2, p. 1412) that systematic study might "turn up a source of rhenium not now guessed."

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TABLE 3

Name of product	Rhenium content, ppm
Sulfidic copper ore	4–5
Copper concentrate	~ 40
Lead concentrate	~ 25
Tails of beneficiation mill	1–1.5
Matte	~ 20
Waste slag	4
Ash of reverbatory furnace, opening 12	~ 20
Dust of blue walls of reverbatory furnace near tubes	~ 50–100
Crude copper	—
Converter dusts from chamber	~ 80
Converter dusts from tubes (discharge)	~200

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DISCUSSIONS

MONAZITE-BEARING PEGMATITES IN THE SOUTH GEORGIA PIEDMONT

In volume 54, pp. 1309–1311 of this journal, Mr. Fortson and Mr. Navarre reported on "Monazite-bearing Pegmatites in the South Georgia Piedmont." Their report deals, specifically, with two small areas about 3½ miles southwest of Culloden. At the first locality, according to Mr. Fortson and Mr. Navarre, there is "an elongated semi-concordant pegmatite" of unknown dimensions in sheared biotite gneiss. At the second locality there are two types of occurrence: (1) scattered semi-concordant pegmatite veinlets, and (2) "a weathered bank in which larger crystals of monazite definitely cut across the foliation and had no other mineral associates." At both localities, they report, the pegmatites are in shear zones "in a complex series of what in many places appears to be metamorphosed volcanic rocks. . . ." Mr. Fortson and Mr. Navarre imply that monazite occurrences are rare in this part of Georgia and that "geologic relations are obscure."

An independent investigation hardly corroborates this report. First of all, monazite-bearing rocks are abundant in this and other parts of Georgia (1). The monazite is found typically as an accessory mineral of microscopic size but up to 0.5 mm across in biotite gneisses—particularly migmatites or lit-par-lit gneisses. The crystals are regularly distributed in some of the biotite gneisses, but in the migmatites or lit-par-lit gneisses they are typically concentrated in the quartz-feldspathic bands and are generally coarser (crystals up to 4 mm across). The pegmatites related to these gneisses generally also bear monazite.

At the first locality mentioned by Fortson and Navarre (Fig. 1) the monazite is concentrated in a narrow pegmatitic band about 25 feet wide by 150 feet long in biotite gneiss. This band differs from the enclosing gneiss only by a somewhat coarser average grain size and more prominent gneissic structure. It is composed of the same minerals as the enclosing gneiss, and its boundaries are not distinct. It is best described as a pegmatitic zone. Contrary to the report of Fortson and Navarre, neither it nor the bounding gneiss reveals any evidence of unusual shearing (they do not even look sheared). Due north of locality 1 about 350 feet is another pegmatitic mass (not mentioned by Fortson and Navarre), which is larger than the first and irregular in shape but also marked by a radiation high (Fig. 1). The geologic map (Fig. 2) shows clearly that both pegmatitic masses are in a plunging anticline. They are not in a shear zone.

The gneiss at this locality is composed of coarse, irregularly shaped perthite and dark red-brown biotite in a finer matrix of interlocking quartz, plagioclase, and K-feldspar. Variations in grain size and the percentage of biotite and feldspar impart to the rock its gneissic banding. In the biotite are dark pleochroic halos enclosing minute highly birefringent crystals. The

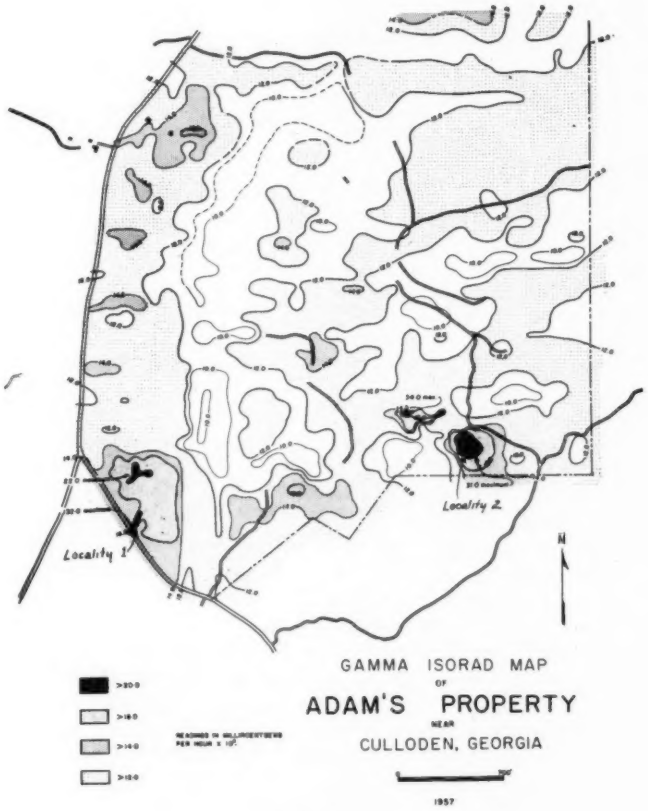

Fig. 1

accessory monazite is pale yellow to pale brown, generally in crystals less than 0.5 mm across in or near biotite. Selected fist-sized specimens contain up to 11 percent monazite; composite samples that are more representative contain 0.07–2.2 percent (spread of five samples). Monazite is not restricted to the pegmatitic band but is also an accessory mineral in the enclosing gneiss.

At the second locality mentioned by Fortson and Navarre the monazite is found in small pegmatitic stringers, lenses, and pods in coronite (not amphi-

bolite!). The presence of monazite in a weathered bank (an excavation in saprolite) generally would not be considered sufficiently different from its presence in the underlying, less weathered rock, to warrant mention as a separate and significant type of occurrence. The largest monazite crystals at this site are less than a quarter inch across; whether they definitely cut across

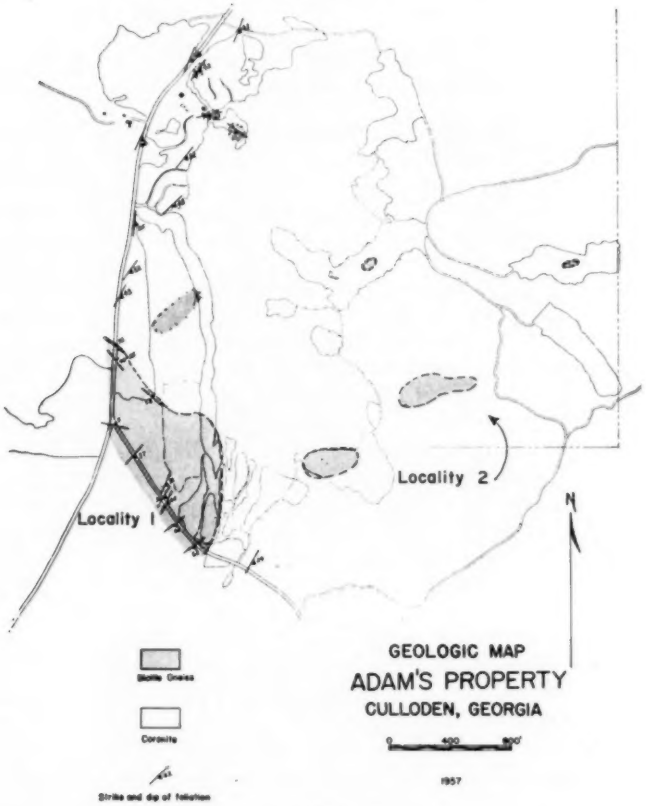

Fig. 2

the foliation as stated by Fortson and Navarre might be true, if there is a foliation in the pegmatitic stringers. Their assertion that the monazite crystals "had no other mineral associates" is harder to accept.

The complex series Schist-Gneiss-Amphibolite of Fortson and Navarre is resolved by a little geologic mapping to biotite gneiss and coronite. Both rocks have been locally pegmatized (incipiently migmatized?). The coronite is a medium- to coarse-grained rock consisting of pyroxene, plagioclase, horn-

blende, and garnet: thin garnet coronas enclose hornblende coronas, which in turn enclose pyroxene cores. These rocks are classic examples of coronite. They are not properly called amphibolite. In view of their coarse grain size and coronal texture, both clearly visible to the unaided eye, they are hardly metamorphosed volcanic rocks.

The rhyolite, phyllite, and angular fragments of possible pyroclastic origin reported by Fortson and Navarre were completely overlooked when the detailed field work on which this note is based was done. Distinctive rocks like rhyolite and phyllite would be expected to stand out conspicuously against the usual coarse-grained high grade metamorphic rocks of the Culloden area. A reexamination has not disclosed either of these rocks, and it is suggested that they must be exceedingly rare, if present.

VERNON J. HURST

DEPT. OF MINES, MINING AND GEOLOGY,
ATLANTA, GEORGIA.
December 13, 1959

REFERENCE

1. Mertie, John B., Jr., 1953, U. S. G. S. Circ. 237.

MONAZITE-BEARING PEGMATITES IN THE SOUTH GEORGIA PIEDMONT—A REPLY

Sir: Sometimes in attempting brevity, data are omitted that may permit misinterpretation. Such is the fact as regards several points in the paper (3) discussed by Dr. Hurst. First, the writers did no detailed work, either structural or petrographical in the Culloden area. The article was purposely submitted under "Scientific Communications" for this reason. On the other hand, it was considered of sufficient interest to call to the attention of others and to invite more detailed work, such as Dr. Hurst has done.

In paragraph one of Dr. Hurst's discussion, apparently no disagreement exists, although the last sentence needs clarification. The sentence reads: "Mr. Fortson and Mr. Navarre imply monazite occurrences are rare in this part of Georgia and that geologic relations are obscure." The paucity of monazite was not under discussion and there was no statement or implication intended that would limit or enlarge the commoness of its occurrence. It was stated (3, p. 1309, paragraph 2) that a few monazite *pegmatite* occurrences are known in the "monazite belts" of Mertie (4). The other part of the sentence, quoted above (". . . geologic relations are obscure"), was taken from another connotation and paragraph in which reference was made to the relationship of mica pegmatites of the Thomaston-Barnesville district and the monazite pegmatites under discussion.

Dr. Hurst's second paragraph reads, in part, ". . . monazite bearing rocks are abundant in this and other parts of Georgia." Reference is made to Mertie (4) who mentioned only one monazite occurrence near the district under discussion and this is ten or more miles northwest of Adam's property (4, p. 26). If others are known in the Culloden district (and they doubtless

exist), the writers would like to know of them. Until such occurrences are published, however, they must conclude that the remainder of Dr. Hurst's second paragraph is concerned with monazite areas not as yet disclosed.

Dr. Hurst, in his third paragraph, discusses pegmatization and shearing at location 1. The writers do not consider that there is any major disagreement regarding pegmatization, be it a zone or a body. Concerning shearing, it is to be pointed out that the writers did not use the term "shear zone" in the sense of LaForge (1). The writers agree with Dr. Hurst that there are local undulations in the country rock. At the same time, it is thought that the area under discussion has been subject to shearing stresses. Surely Dr. Hurst did not intend to imply any lack of compatibility between shearing and anticlinal folding. Concerning the statement that the rocks "don't even look sheared," Fortson has seen rock near this area that looks like massive quartzite, but microscopic examination reveals mylonitic texture. It doesn't "look sheared" either.

Attention is called to the shearing in the mylonite noted in the southeast corner of the map (3).

Also, with reference to the third paragraph, the writers are glad to see that detailed work has revealed another monazite locality. More work of this quality would probably uncover additional monazite occurrences in adjacent areas.

The fourth paragraph confines itself entirely to some of Dr. Hurst's own work.

Dr. Hurst's fifth paragraph contains three points that need clarification: (1) concerning the importance of reporting monazite crystals in the weathered rock at Site 2, it should be stated that the largest crystal found by Navarre was approximately 2×1 inch; it will be noted from the original article that the area has been excavated since the discovery of these crystals, therefore, it is quite possible that Dr. Hurst did not find crystals larger than $\frac{1}{4}$ inch when he was on this property; (2) crystals *were found* oriented transverse to the foliation of the enclosing rock; (3) the statement concerning the mineral association refers to the saprolitic remains of the original rock; there was no evidence of quartz or kaolin, which should have been present in a decomposed acid pegmatite; unquestionably, there were other minerals associated with the original occurrences of the monazite but they were not distinguishable when the crystals were discovered.

In reply to Dr. Hurst's sixth and seventh paragraphs, the writers do not think that the area labelled "Schist-Gneiss-Amphibolite" is as simple as indicated. It should be re-emphasized that the writers' work was not detailed and the note was based on field evidence only. The discussion of paragraphs six and seven may be broken into three parts: (A) the term amphibolite was chosen because the field identification fits descriptions as noted in the following publications: Turner & Verhoogen (5), Tyrrell (6), and Williams, Turner, Gilbert (7), as well as the definition in *The Glossary of Geology* (1); (B) meta-volcanic rocks were not seen in the immediate vicinity of the monazite occurrences; approximately 2.1 miles N 80° E of the center of Culloden a small outcrop of massive, aphanitic, dark-grey rock (meta-rhyolite or fine-

grained felsic meta-sediment?) is exposed on the north side of Georgia 74; the rock is hard to break with a hammer and has conchoidal fracture; an exposure in a road 1.4 miles S 10° W of Pleasant Hill reveals an "augen gneiss," where unsheared is seen to be a breccia (in part of pyroclastic origin?); (C) amphibole-bearing rocks, in which coronas have been described, are called "charnokites" in the Thomaston Quadrangle (2), a few miles west of the area under discussion; a discussion of coronites in Georgia, although interesting, was purposely avoided.

As already stated, the purpose of the original paper was not to report detailed studies, but to invite detailed studies.

CHARLES W. FORTSON, JR.
ALFRED T. NAVARRE

GEORGIA INSTITUTE OF TECHNOLOGY,
ATLANTA, GEORGIA,
Feb. 24, 1960

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THE SOURCE BED CONCEPT[1]

Sir: Messrs. Murray, Carter and Hall (ECON. GEOL., Vol. 54, No. 5, 1959) have offered a lengthy criticism of some aspects of my discussion on C. L. Knight's paper "The Source Bed Concept" (ECON. GEOL., vol. 53, No. 7, 1958). While I appreciate the danger that the theme of the original paper can become lost in side issues, yet the discussion by Murray et al does call for reply.

My remarks regarding mineragraphic evidence were certainly not meant in the context accepted by Murray et al, but were simply meant to imply that mineragraphic evidence is not necessarily the final answer. It must be considered in association with other data. I pointed out that such laboratory data—dealing mostly with magmatic origin of ores—are at present far more voluminous and more correctly documented than are routine field observations or material pertaining to syngenesis. These latter do not attract so much attention; they do not have, if the expression may be pardoned, any aura of wizardry. The point to be made is that one aspect of a problem must not be allowed to dominate other aspects. I am not impressed by Murray et al's statement that the idea of syngenesis at Mount Isa was discussed and rejected "more than 20 years ago."

[1] Published with the permission of the Director, Bureau of Mineral Resources.

Murray et al. have correctly pointed out that I do not have an intimate knowledge of the mine geology; but I have not anywhere attempted to discuss the geology of Mount Isa mine in detail. I did not anywhere lay claim to being the first to suggest that sedimentary structures existed at Mount Isa. However they were most certainly not demonstrated to me as such and I know of a large number of people who were not aware of their presence. Since my last visit to the mine over two years ago, the idea of such features has become quite popular (or unpopular) and I did have something to do with bringing the matter to the attention of a number of interested people. In regard to Murray et al's statement that they "do not concede that Mount Isa crenulations and breccias are examples of primary slump structures" Figure 1 is offered to the reader for inspection. (As Murray et al. correctly point out, these

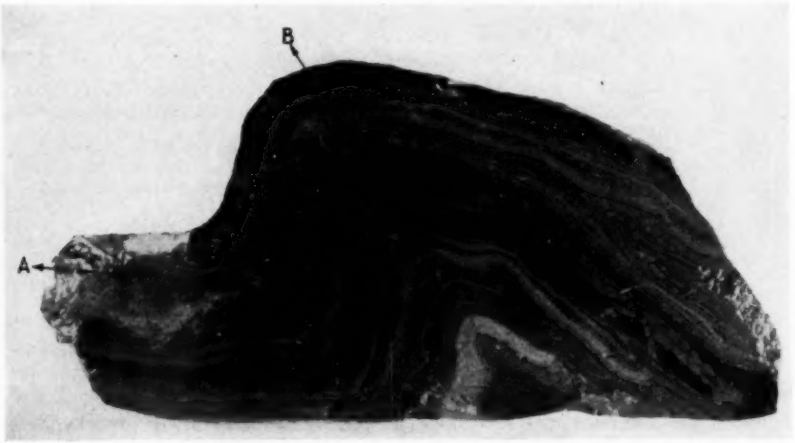

FIG. 1. Finely laminated sulfide (galena, sphalerite and pyrite) ore, Mt. Isa mine, showing a primary slump nappe modified by a secondary fold. (A) indicates direction of slumping (up dip in this case); (B) the axis of the secondary (tectonic) structure.

features are quite "photogenic"—unfortunately the equally convincing breccias are not.) I interpret this as a slump nappe modified by later tectonic movement. The reader can form his own opinion.

There is neither any reason for surprise nor for excitement about the presence of such features; on the contrary, it would be most surprising if, in a lithology such as the Mount Isa Shale, such features were not present. They do become important in their bearing on the origin of the deposit: but I did not anywhere set out to prove that the Mount Isa deposits were syngenetic, whatever my own personal opinion may be. I am therefore puzzled by Murray et al's final remark that I have "picked a poor example in trying to fit the unique Mount Isa deposit to (my) theories." I merely pointed out certain features that I continue to believe have not been correctly interpreted and documented, drew attention to others and noted a discrepancy in age

that is relevant, in support of a general plea for more careful documentation of features pertaining to syngenesis. This does not constitute a "theory" but rather, I hope, an earnest desire to see more such material in the literature in order that in the foreseeable future we might be able to rely more on a balance of facts and less on philosophy or tradition.

Mr. Carter and his staff receive and deserve every credit for the fact that their exploratory work at Mount Isa mine has resulted in very large increases in the mines reserves over the past few years. However, it is an aphorism that the geometry of a known deposit can be established without the reasons for such geometry being fully understood; and as one of many who are interested and participating in the search for new deposits, Messrs. Murray, Carter and Hall will, I hope, excuse me if I continue to question certain aspects of the currently available, published data on their mine.

B. P. WALPOLE

BUREAU OF MINERAL RESOURCES,
CANBERRA, AUSTRALIA,
Jan. 11, 1960

STRUCTURAL HISTORY OF THE BEAVERLODGE AREA[1]

Sir: A letter by Hill (ECON. GEOL., vol. 54, no. 8, p. 1577) raises several questions concerning my paper of the above title (2). First, Hill states that the structural history of one fault is not a structural history of the whole Beaverlodge area. This seems, by itself, a reasonable statement and may have been brought on by the fact that I devoted considerable space to discussing movement on the St. Louis-ABC fault. However, I am disheartened to think that, because I did so, Hill missed my remarks concerning the Black Bay fault (p. 482, 487, 488, 489, 490, 493) as well as the descriptions of schistosity, major and minor folds, stratigraphic relations and interpretations thereof (p. 479, 480, 492).

Second, Hill mentions two faults, not described in my paper, that "show right-handed movement of 1,000 to 1,200 feet." The wording here is unfortunate. Hill should have seen to it that "right-handed movement" was preceded by the word "apparent." His original measurements (4) consisted of taking the separation between doubtfully equivalent Tazin rocks along lineaments of uncertain or unknown dip. Actually, Hill's faults seem typical of hundreds of minor breaks in the area. Where it is possible to work out relative slip movements, these are generally less than 150 feet.

Third, Hill asks, "What evidence exists for the 'reactivation of stresses' and the 'late change in direction of force suggested by cross-folding' of Table 1?" I am puzzled by this as the answer seems embodied in the question; i.e., cross-folding suggests (although it does not prove) a subsequent change in direction of compression. If Hill means to ask for the evidence of cross-folding itself, this is given on page 480.

Hill closes with the statement that a footnote in my paper drawing attention to a discussion by Gussow (3) would have been appreciated. As my paper had been in press for six months prior to publication of Gussow's work, I am not sure that Hill's request for a footnote is reasonable. Apart from

[1] Published by permission of the Director, Geological Survey of Canada.

this, however, I feel obliged to point out that Gussow's paper, although it is a stimulating discussion of some of the correlation problems of the Athabasca series, contains certain misinformation on the structure of the Beaverlodge area. For example, Gussow depicts the Black Bay and St. Louis faults as regional thrusts, dipping north (p. 8, 9, 14), whereas these are both regional normal faults that do, in fact, dip south.

J. A. CHAMBERLAIN,
GEOLOGICAL SURVEY OF CANADA,
OTTAWA, ONTARIO,
Feb. 6, 1960

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ILMENITE ALTERATION UNDER REDUCING CONDITIONS IN UNCONSOLIDATED SEDIMENTS[1]

Sir: The report of experimental alteration of ilmenite to rutile and pyrite in the presence of H_2S by Gruner (3) is of considerable interest in the study of heavy residues of sediments deposited in a reducing environment. Ilmenite in certain bauxites may also have been altered under reducing conditions. Recently I examined a number of heavy residues from samples of unconsolidated sediments of the nonmarine Cretaceous group in the Maryland Coastal Plain. The samples were obtained in the course of a cooperative investigation of clays by the Maryland Geological Survey, the U. S. Geological Survey, and the U. S. Bureau of Mines. These sediments contain authigenic titanium minerals as well as pyrite and siderite.

Sands and clays derived from deeply weathered crystalline rocks were deposited in swamps and lagoons by rivers draining part of the Appalachian region. The swampy conditions provided a reducing environment. Some of the heavy residues from these sediments contain authigenic rutile as encrustations on, and as recrystallizations of, the edges of ilmenite grains. Some ilmenite grains are almost completely replaced by a dark-brown resinous mineral that was identified as rutile. Other ilmenite grains have light-yellow patches and strings of anatase on their surfaces. Pyrite is present in about one-fifth of the 300 samples examined, and although it is generally in small, well-crystallized cubes and pyritohedra, some of it encrusts ilmenite suggesting that it has formed from the ferrous iron of the ilmenite. Authigenic anatase and brookite occur in small amounts in many of the samples. Anatase is more plentiful than brookite.

Titanium minerals occur in most bauxites and laterites. The terra rossa type of bauxite that originates by the alteration of clay in a limestone environ-

[1] Publication authorized by the Director, U. S. Geological Survey.

ment contains, on the average, 2 percent TiO_2 as anatase, rutile, and brookite that have crystallized authigenically. Some of the Hungarian bauxites studied by Bárdossy and Bárdossy (1) were originally associated with swamp conditions that produced pyrite. Siderite is present in the redeposited bauxite of Arkansas described by Gordon and others (2). Bárdossy and Bárdossy (1, p. 201) mention that Ti^{3+} may be present in reducing conditions, although Ti^{4+} is the usual valence state in most natural situations. Shtcherbina (6) indicated that both Ti^{3+} and Ti^{4+} may be present under conditions in which Fe^{2+} is stable. Latimer (5, p. 267) shows that equal concentrations of Ti^{3+} and Ti^{4+} may be present in 4.1 *N* H_2SO_4 where $E^\circ = -0.056$ v. The reaction $Ti^{3+} + H_2O = TiO^{2+} + 2H^+ + e^-$ takes place at $E^\circ = -0.1$ v (5, p. 342). Gruner's (3) second equation, $FeS + H_2S \rightarrow FeS_2 + H_2$ provides conditions under which the change of Ti^{3+} to TiO_2^{2+} can occur. The redox potential of environments in which siderite and pyrite are crystallizing is between Eh = −0.1 and −0.3 (4, p. 26). The amount of reduction of Ti^{4+} to Ti^{3+} in an environment with siderite and pyrite at pH 3 and pH 4 was calculated by the Nernst equation to be:

PERCENTAGE OF Ti^{4+} REDUCED

	pH3	pH4	
Eh, −0.1	0.3	0.002	(siderite environment)
Eh, −0.3	84	5	(pyrite environment)

The swamp environment of the Cretaceous nonmarine sediments on the Maryland Coastal Plain had a redox potential of between −0.1 and −0.3 as shown by the presence of siderite and pyrite. The pH was probably about 3 to 4 because many of the clays are now acid (John W. Hosterman, U. S. Geological Survey, oral communication). This environment was therefore one in which the alteration of ilmenite to rutile and pyrite could occur. However, it is unlikely that more than a small part of the total pyrite present was formed in this way because ilmenite is not abundant in these sediments. Also most of the iron was released from adhering ferric oxide on the clay particles. Reducing conditions may have an important effect on the alteration of iron-bearing detrital minerals such as garnet, amphiboles, and staurolite in sands or clays in which pyrite and siderite occur but this has not yet been studied.

DOROTHY CARROLL

U. S. GEOLOGICAL SURVEY,
WASHINGTON 25, D. C.,
Feb. 22, 1960

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Economic Geology
Vol. 55, 1960, pp. 620–622

REVIEWS

Boston, A Topographical History. By WALTER MUIR WHITEHEAD. Harvard University Press, 1959.

The word topographical in the title calls for brief mention of this attractive book. But lest geomorphologists become overintrigued, one should hasten to note that the topographic changes are mainly man-made and the history begins in 1632 except for passing reference to Irving Crosby's geological studies. Many quaint and interesting maps are reproduced as well as a host of illustrations of colonial and more modern buildings. Had the maps been redrawn by a geologist they would have constituted an attractive and legible chronological series on uniform scale and orientation depicting the progress in filling in of the Mill Pond and the Back Bay. But few geologists or geographers could have written such a charming story of the growth from a cluster of houses at the base of Tramountain to a metropolitan city.

H. E. MCKINSTRY

General Crystallography: A Brief Compendium. By W. F. DE JONG. Pp. 281; figs. 231; tables 41. Translated from Dutch edition of 1951, with emendations and additions, by Miss J. Pouwelson and Messrs. T. McClintock and N. F. M. Henry. W. H. Freeman & Co., San Francisco, 1959. Price, $6.00.

The subtitle describes this book perfectly. Part I (p. 1–92), geometric crystallography, contains brief but very good sections on description, calculation, drawing, and goniometric determination of crystals. Part II (p. 93–134), structural crystallography, contains an historical note and sections on structure theory, and the determination of crystal structure. Part III (p. 135–186), chemical crystallography, discusses bonds, particles, and structures, both in general and in particular. Part IV (p. 187–266), physical crystallography, contains phenomenological and explanatory sections covering important properties.

This book appears to be a practical, albeit very condensed summary of the present state of the science (and art) of crystallography. Nearly any one would find it an important and useful reference for individual study, and if supplemented and perhaps leavened by suitable lecture material it might be useful as a textbook. The translation team are to be commended for their excellent work.

H. WINCHELL

Principles of Geology. By GEORGE W. BAIN. Pp. 563. Lithoprinted at Edwards Bros., Ann Arbor, Michigan, 1959.

This is quite an unusual elementary textbook in many ways. The author states on page on: "The treatment of Principles of Geology is novel for contemporary textbooks in procedural form, scientific content, and in many arbitrary decisions." The first three pages explain the form. There are five main sections: I, The Study Called Geology (9 p.); II, Gradational or Destructive Activity; III, Consolidation

of the Record; IV, Restorative or Constructional Activity; V, Geology in Human Affairs; VI, Appendices. Each section has its own table of contents; and each subsection has its separate table of contents, all indicated by numbers and letters. Footnotes are carried at the bottoms of the pages to indicate supplementary reading. The extensive use of main, subheadings, and marginal subheads gives a somewhat jerky impression to the reader. There are a large number of excellently chosen line drawings but unfortunately many of them are over-reduced.

The subject matter is that generally included in elementary textbooks and includes many of the author's own observations gleaned from wide travel. The section on Geology in Human Activities includes much interesting material not ordinarily found in elementary texts. The appendices (wrongly paginated) include minerals, rocks, the story of a region (Van Horn, Texas), and geologic time scale.

Physics and Geology. By J. A. JACOBS, R. D. RUSSELL and J. TUZO WILSON. Pp. 424. McGraw-Hill Book Co., New York, 1959. Price, $9.75.

The authors in this book draw upon geophysics, geology, and geochemistry to describe the nature, composition, and behavior of the earth. The book is planned to give students of geology some idea of the physics of the earth and to give other scientists a knowledge of geology in relation to geophysics. The book is an outgrowth of courses given to senior undergraduates and graduate students in the Departments of Physics and of Geology at the University of Toronto.

The 17 chapters cover: The Universe and the Solar system, seismology, composition of the earth, gravity, thermal history, geomagnetism, upper atmosphere, geochronology, isotope geology, dynamics, ocean floors, inactive mountains, origin of earth surface features, and glaciology. Six appendices contain supplementary material. Lists of suggested readings follow each chapter. The book is quite broad in its scope.

The book is well integrated, well written, and well illustrated. It should serve as a valuable text and reference.

Igneous and Metamorphic Geology, 2nd Edit. By FRANCIS J. TURNER and JOHN VERHOOGEN. Pp. 694; figs. 115. McGraw-Hill Book Co., New York, 1960. Price, $12.00.

The first edition of this book has become a worldwide standard reference for advanced students, research workers, and teachers in petrology. This second edition has been considerably revised and incorporates recent developments in petrology and geochemistry. It now contains 24 chapters, an increase of 2 chapters over the first edition, and contains 92 more pages. The first 12 chapter headings are identical with the first edition. Chapter 13, on Nepheline Syenite, Ijolites, and Carbonatites is new, as is Chapter 17, the Chemical Principles of Melamorphism, and Chapter 19, Facies of Contact Metamorphism. The section on igneous petrology has been expanded and summarizes the important experimental work in this field since 1954. Much new data are included on the chemical composition and distribution of minor elements in igneous rocks. The discussion of metamorphic facies has been expanded to give up-to-date treatment of recent experimental data. Also Chapter 23 on fabrics has been revised to conform with newer experimental data, especially on marble. Numerous other changes occur in the chapters that still carry the same headings.

This edition is comprehensive and gives considerable attention to equilibrium and stability; balance is made between field, petrographic and experimental data.

Every student of hard rock geology will need to have a copy of this revised and expanded edition.

Mineral Equilibria, at Low Temperature and Pressure. By ROBERT M. GARRELS. Pp. 254. Harper & Bros., New York, 1960. Price, $6.00.

Dr. Garrels has brought together in this volume information from widely scattered sources that has been appearing in increasing amount in geologic journals that use solution chemistry. He includes practically all of the diagrams that have appeared in the scientific literature along with many new ones including his own. The reader is presented in detail with the methods of construction of the diagrams and the calculations required. He can with a modest background of chemistry be able to understand the diagrams and even to make similar ones showing relations in systems of his own choice.

The subject matter deals largely with chemical relations in aqueous solutions at low temperature and pressure. He introduces the reader to methods of representing mineral equilibria in pH potential diagrams. He stresses, however, individual equations rather than rectilinear graphs or triangles in showing equilibrium relations among minerals, a field in which he has done much himself.

The 7 chapters consist of Introduction, Activity-Concentration Relations, Carbonate Equilibria, Measurement of Eh and pH, Partial Pressure Diagrams, Eh-pH Diagrams, Geologic Applications of Eh-pH Diagrams. An appendix of 21 pages gives free energy of formation of compounds, gases, and ions. Each chapter carries a list of selected references.

The chapter of greatest interest to geologists deals with the author's geologic applications of Eh-pH diagrams. In this he uses as examples mine water, sedimentary iron and manganese deposits, secondary enrichment of ores, weathering of uranium deposits, oxidation of sulfide ores, marine chemical sediments, and the environment of ore deposition.

The treatment is such that the book may be used by the student, the professional, and the general reader. It will prove of great value to the geologist because information that he might have to search out for himself is conveniently assembled and well presented in this single volume.

BOOKS RECEIVED

JOHN E. COTTON AND CYRUS W. FIELD

Elements of Cartography, 2nd Edit. ARTHUR H. ROBINSON. Pp. 343. John Wiley & Sons, New York, 1960. Price, $8.75. *Mostly rewritten. Mapping, planning, designing and construction of maps and projections; lettering; convenient guide to making maps.*

Petrology Condensed and Simplified. GURDON MONTAGUE BUTLER. Pp. 31; figs. 2; tbls. 2. Price, 50 cents. University of Arizona Bulletin, Vol. XXX, No. 1, Tucson, 1959. *A brief description of the major rock types.*

The Australian Mineral Industry, 1958 Review. Pp. 240; figs. 6; tbls. 343. Price, 12/–. Bureau of Mineral Resources, Geology, and Geophysics, Melbourne, 1959. *The mining industry maintained a rather high rate of production in 1958. Production of tungsten, rutile, zircon, lead, and zinc was less than in 1957. In part this was a reflection of the recession in the United States.*

Belgian Congo. Geological Survey Sheets in color. Scale 1:50,000. **Yak.** S. 6/15, N.W. 1, N.W. 2, N.W. 3. *Part of new geologic map of the Congo.*

Geology of the Country around Polonnaruwa, Ceylon. PIYADASA W. VITANAGE. Pp. 75; pls. 12; figs. 11; tbls. 12. Map, scale 1:63,360. Geological Survey of Ceylon Memoir No. 1, Colombo, 1959. *With the exception of a few mica-bearing pegmatites no minerals of economic importance were found during this study. Granite and gneiss are available for road metal and building stone. Limestone is of potential economic value.*

Petrology of the Fountain and Lyons Formations, Front Range, Colorado. JOHN F. HUBERT. Pp. 242; figs. 71; tbls. 40. Price, $3.00. Quarterly of the Colorado School of Mines, Vol. 55, No. 1, Golden, 1960. *Stratigraphy, lithology, and petrography are used to interpret the sedimentary history of the formations.*

Summary of Progress of the Geological Survey of Great Britain and the Museum of Practical Geology for the Year 1958. Pp. 77; tbls. 5. Price, 5 sh. Department of Scientific and Industrial Research, London, 1959. *Aeromagnetic surveys have discovered several prominent magnetic anomalies, such as over the Askrigg Block and in the Irish Sea between Furness and the Isle of Man.*

On the Inai Group of the Lower and Middle Triassic System; On Some Triassic Ammonites from the Rifu Formation. YOSHIO ONUKI and YUJI BANDO. Pp. 80; pls. 11; figs. 24; tbls. 12. Institute of Geology and Paleontology Tohuku University Contribution 50, Sendai, Japan, 1959. *In Japanese; English summaries.*

Kumamoto Journal of Science, Series B, Section 1: Geology. Vol. 3, No. 2. Pp. 40; figs. 21; tbls. 10. Kumamoto University, Kumamoto, Japan, 1959. *Five articles by R. Saito dealing with the stratigraphy of Burma, and an article by K. Yamoaka on garnet from Toroku Mine. In English.*

Geology of the Isles of Shoals. KATHERINE FOWLER-BILLINGS. Pp. 51; figs. 25. New Hampshire State Planning and Development Commission, Concord, 1959. *A non-technical pamphlet. Rocks that crop out on the islands are tentatively considered to be correlative with the Paleozoic rocks of the New Hampshire coast.*

Regional Gravity Map of Northwestern North Dakota. MILLER HANSEN. North Dakota Geological Survey, Grand Forks, 1960.

Oklahoma Geology Notes, Vol. 20, No. 2. Pp. 43; figs. 10. Price, 25 cents. Oklahoma Geological Survey, Norman, 1960. *Three short papers and five notes. One paper deals with the Permian salt beds in the Laverne Gas Area.*

Fifth Annual Report of the Ontario Fuel Board (1958). Pp. 140; figs. 2; tbls. 22. Toronto, 1959. *Includes sections on the natural gas industry, the petroleum industry, reserves of oil and gas, exploration and drilling, and well logs.*

Annual Report of the Geological Survey Department—April 1958–March 1959. Pp. 22; tbl. 1. Price, Shs. 2/–. Somaliland Protectorate, Hargeisa, 1959. *Petroleum prospecting was carried on by three companies. The Survey continued the search for economic mineral deposits.*

California Division of Mines—San Francisco, 1959.

Bull. 146. Geology and Mineral Deposits of the Lake Elsinore Quadrangle, California. RENÉ ENGEL, THOMAS E. GAY, JR., and B. L. ROGERS. Pp. 154; pls. 7; figs. 24. Price, $2.50. *Metallic resources include arsenic, gold, copper, lead, silver, zinc, manganese, and tin. The Good Hope gold mine is in this area. During the last 50 years clay has been the most important mineral commodity.*

Special Report 57. San Francisco Earthquakes of March 1957. GORDON B. OAKESHOTT, EDITOR. Pp. 127; figs. 58; tbls. 9; photos 51. Price, $1.25. *Eight papers concerning the earth quakes, such as information on the San Andreas Fault, seismic history of the area, intensity and ground motion of the earthquake on March 22, and damage to buildings, etc.*

Special Report 59. Mineralogy of Beach Sands Between Halfmoon and Monterey Bays, California. C. OSBORNE HUTTON. Pp. 32; figs. 5; tbls. 13. Price, 50 cents. *In most instances the heavy minerals in the sands have been derived from rock types located in the drainage areas of local streams reaching the Pacific.*

Geological Survey of Canada—Ottawa, 1959–60.

Paper 59–10. Rare Earths of the Grenville Sub-Province, Ontario and Quebec. E. R. ROSE. Pp. 41; tbls. 7. Price, 25 cents. *The most promising known sources of rare earths in Canada appear to be the uranium deposits of the Blind River and Bancroft areas and the niobium deposits of the Oka and Lake Nipissing areas.*

Bull. 50. A Glacial Study of Central Quebec-Labrador. E. P. HENDERSON. Pp. 94; pls. 24; figs. 11. Price, $1.00. *A detailed study of part of the Labrador lake plateau including a large section of the central elevated area of the peninsula.*

Bull. 52. Palaeoecology of the Marine Pleistocene Faunas of Southwestern British Columbia. FRANCES J. E. WAGNER. Pp. 67; pl. 1; fig. 3; tbls. 20. Price, $1.00. *At least three major glaciations affected southwestern British Columbia.*

Bull. 55. Fossil Bibionidae (Diptera) from British Columbia. H. M. A. RICE. Pp. 37; pls. 4; figs. 8; tbls. 3. Price, $1.00.

Geological Survey of Canada Aeromagnetic Maps. Scale 1:63,360. *Nova Scotia—Church Point, 611G; Digby, 771G; Bridgetown, 782G. New Brunswick —Petitcodiac, 769G; Campobello, 773G; Loch Lomond, 776G. Nikip, Windigo, Shinbone, McCauley, Whitestone, Cat, Zionz, Wesleyan, and Otatakan Lades, and Anenimus River in Kenora District, Ontario; Cape Spencer, Rogersville, Harcourt, Salisbury, Grand Manan, and St. George in New Brunswick; Meteghan, Ecum Secum, Bay of Fundy, Hopewell, and New Glasgow in New Brunswick; Miette, in Alberta; Sandy Lake and St. Johns, in Newfoundland; and Wholdaia, in N. W. Territories; Surficial Geology of Oyster River, in British Columbia; geology of Kennetcook and Shubenacadie in Nova Scotia.*

Mineral Information Bull. MR 34. A Survey of the Uranium Industry in Canada. J. W. GRIFFITH. Pp. 94; figs. 7; tbls. 4. Price, 50 cents. *The value of uranium produced in 1958 exceeded that of any other metallic mineral. The Blind River district produced 68 percent of the total concentrates.*

Egypt—United Arab Republic—Geological Survey, Cairo, 1958–59.

Geology of El-Daghbag—El-Gindi District (Barramiya East and Barramiya West Sheets). F. AMER and A. O. MANSOUR. Pp. 79; figs. 10. Price, P.T. 145. *General geology, geologic map (1:100,000) of metamorphic and igneous rocks; gold-bearing quartz veins, and marble. In English.*

Seven New Occurrences of the Igla Formation in the Eastern Desert of Egypt. M. K. AKAAD and M. F. EL-RAMLY. Paper No. 3. Pp. 38; figs. 5. Price, P.T. 40. *Late Precambrian unmetamorphosed red beds.*

The Miocene in the Gulf of Suez Region (Egypt). H. SADEK. Pp. 111; figs. 7. Tectonic map, scale 1:1,000,000. Geologic map, scale 1:500,000. Price, P.T. 100. *Miocene stratigraphy tectonics, and geologic history of the Gulf of Suez region.*

Ontario Department of Mines—Toronto, 1960.

Sixty-Seventh Annual Rept., Vol. LXVII, Pt. 2, 1958. Mining Operations in 1957. DORIS J. FIELD. Pp. 183; tbls. 237. *A record of mining activity listed according to minerals or elements produced.*

Sixty-Ninth Annual Rept., Vol. LXIX, Pt. 3, 1960. Geology of the Saganash Lake-Wakusimi River Area. R. C. MCMURCHY. Pp. 19; fig. 1; photos. 5. Map, scale 1:63,360. *Recent surveys have shown that volcanic and sedimentary rocks are more extensive than previously realized. More prospecting is needed.*

Quebec Department of Mines—Quebec, 1959.

Geological Rept. 90. Richard-Gravier Area, Gaspé Peninsula. C. CARBONNEAU. Pp. 63; pls. 8; figs. 5; tbls. 4. Map, scale 1:63,360. *This area is just south of the base metal deposits of Lemieux township and may hold some promise for future exploration.*

The Mining Industry of the Province of Quebec in 1958. Pp. 136; pls. 8; fig. 1; tbls. 65. *The value of mineral production of Quebec was 12 percent less in 1958 than in 1957. Metal producers were affected the most by the recession of 1957–1958.*

Geological Survey of Japan—Hisamoto-cho, Kawasaki-shi, 1959.

Explanatory Text of the Geological Map of Japan. Toga & Funakawa (Akita-1, 2). KAZUO HUZIOKA. Pp. 67; figs. 4; tbls. 14. Maps, scale 1:50,000. *These areas represent the western portion of the Akita oil field. Oil-bearing strata are the lower three formations of the Funakawa group of later Miocene and earlier Pliocene age. In Japanese; English abstract.*

Explanatory Text of the Geological Map of Japan. Kodomari (Aomori-10). KONROKU TSUSHIMA and FUJIO UEMURA. Pp. 37; figs. 2; tbls. 3. Map, scale 1:50,000. *Volcanic rocks in this area are slightly mineralized but deposits are not of economic importance. In Japanese; English abstract.*

Rept. 183: Genetic Studies of Natural Gas Accumulations. KOJI MOTOJIMA. Pp. 57; pls. 12; figs. 27; tbls. 16. *Gas accumulations in peat-bogs of central Ishikari plain were studied in order to determine the relation of chemical components of the peat and groundwater at any given depth, and to note the chemical changes or vertical distribution changes of chemical components with time. In Japanese; English abstract and titles to plates, figures, and tables.*

Bulletin of the Geological Survey of Japan, Vol. 10, No. 10. Pp. 102; pls. 12; figs. 71; tbls. 19. *Seven papers are in Japanese with English abstracts and four short notes are in Japanese only. One paper is on the titaniferous iron ore deposits of the Unjo District; another on the fluorite deposit of the Hiraiwa Mine; and a third paper is a groundwater investigation.*

Distribution Map of Oil and Gas Fields in Japan. Scale, 1:2,000,000. *Included charts show production of crude oil and natural gas by the year and the province.*

Pennsylvania Geological Survey—Harrisburg, 1959–60.

Bulletin M41. History, Present Status and Future Possibilities of Secondary Recovery Operations in Pennsylvania. W. S. LYTLE. (Reprinted from Inter-

state Oil Compact Commission Committee Bulletin, Vol. 1, No. 2, Dec. 1959.) Pp. 28–42; figs. 7. *Experiments conducted in Pennsylvania led to the wide-spread use of vacuum, water flooding, and air-gas drive methods for secondary recovery of crude oil. Increased production through secondary recovery will undoubtedly be effected if the market conditions improve sufficiently.*

Information Circ. 16. Catalogue of Deep Well Samples and Geophysical Logs to January 1, 1959. W. R. WAGNER. Pp. 84; pl. 1; fig. 1. *The term "deep well" is arbitrarily chosen to apply to any well which reaches or penetrates the Tully Limestone which is the top of the Middle Devonian; depth is not a criterion.*

Information Circular 17. Geology of a Barite Occurrence, Fulton County, Pennsylvania. ARTHUR A. SOCOLOW. (Reprinted from Proceedings of the Pennsylvania Academy of Science, Vol. XXXIII, p. 204–208). Figs. 5. *Two periods of barite mineralization are represented in a fault zone in the Tonoloway limestone. No significant amounts of sulfide minerals occur.*

Geologic Interpretation of Aeromagnetic Maps. Information Circulars 18–20, 22, 23; Valley Forge, Norristown, Malvern, West Chester, Media, and East Greenville Quadrangles. A. A. SOCOLOW. *Many small anomalies over Wissahickon schist, serpentine, and metamorphic rocks; two large ones in East Greenville over known iron ore.*

Bull. G33. Mineral Collecting in Pennsylvania. DAVIS M. LAPHAM and ALAN R. GEYER. Pp. 74; figs. 31. *A guide for the mineral collector. Gives mineral localities with sketch maps.*

Bull. G32. Fourth Series. Glacial Geology of Northwestern Pennsylvania. V. C. SHEPPS, G. W. WHITE, J. B. DROSTE, R. F. SITLER. Pp. 59; figs. 11. Map, scale 1:125,000. *Ice spread in this area twice during the Illinoian age and five times during the Wisconsin age. Tills of these advances are identified on the basis of leaching, texture, color, and soil profile development.*

Union of South Africa Department of Mines—Pretoria, 1959.

Bull. 29. Northern Natal Coal-Field (Area No. 2) The Utrecht Area. K. H. L. SEHLKE and S. W. VAN DER MERWE. Pp. 125; pl. 1; tbls. 5. Map, scale 1:125,000. Price, 62. 3d. *Part I discusses the general geology, coal seams, natural oil, and reserves. Part II discusses the effect of dolerite on the coal seams, and the characteristics of the seams. 31 drill hole records are included.*

Bibliography and Subject Index of South African Geology 1957. Pp. 60. Price 3s. 6d.

U. S. Geological Survey—Washington, D. C., 1959–60.

Water-Supply Paper 1456. Ground-Water Levels in the United States 1956: North-Central States. PHILIP E. LAMOREAUX, Chief, Ground Water Branch. Pp. 76; figs. 10. Price, 40 cents. *Records for Illinois, Iowa, Kansas, Minnesota, Missouri, Nebraska, North Dakota, South Dakota, and Wisconsin.*

Water-Supply Paper 1485. Quality of Surface Waters for Irrigation Western United States 1956. S. K. LOVE, Chief, Quality of Water Branch. Pp. 185; pl. 1. *Reports from 106 stations west of the Mississippi River.*

Water-Supply Paper 1493. Geologic and Ground-Water Reconnaissance of the Loup River Drainage Basin Nebraska. R. T. SNIEGOCKI and R. H. LANGFORD. Pp. 106; pls. 2; figs. 20; tbls. 12. *Semiconsolidated and unconsolidated deposits of Cenozoic age, which underlie dune sand and loess, contain vast stores of water.*

Bull. 1039-D. Geology and Cement Raw Materials of the Windy Creek Area, Alaska. R. M. MOXHAM, R. A. ECKHART, and E. H. COBB. Pp. 67–100; pl. 1; figs. 5; tbls. 7. *This area on the south flank of the Alaska Range offers at least two limestone deposits suitable for cement-manufacturing purposes.*

Bull. 1055. Uranium in Coal in the Western United States. Pp. 315; pls. 59; figs. 44; tbls. 45; chart 1. *Ten papers on uranium-bearing coals and carbonaceous rocks. Compared with current sources of uranium, most uranium-bearing coal deposits are very low grade. Higher ash content of these deposits also renders the coals less suitable as a fuel.*

Bull. 1059-G. Selected Annotated Bibliography of the Geology of Uranium-Bearing Veins in the United States. BASIL G. DEAN. Pp. 327–440; pl. 1. *Includes 211 references to reports available as of June 1957.*

Economic Geology
Vol. 55, 1960, p. 628

SCIENTIFIC COMMUNICATIONS

HENRY R. ALDRICH, since 1940 chief administrative officer of the Geological Society of America, has retired as secretary, councilor and editor-in-chief of the organization. During his twenty-five years with the Society, Dr. Aldrich has seen it grow from a membership of less than one thousand to 5,316, and a three-fold increase in its scientific publications. He has been succeeded as secretary by Dr. FREDERICK BETZ, JR., who recently returned from Germany, where he served with the Military Geology Branch of the United States Geological Survey. Dr. Aldrich plans to join the staff of Columbia's Lamont Geological Observatory, at Palisades, N. Y. He lives at 200 Van Orden Avenue, Leonia, N. J.

PAUL F. KERR, Newberry Professor of Mineralogy at Columbia University, has been awarded an honorary Doctor of Science degree by Occidental College in Los Angeles, California.

HOLLIS G. PEACOCK has been named to fill the post of Chief Geologist with Utah Construction and Mining Company with headquarters in San Francisco.

DONALD S. SMYTHE has retired as head of the Bear Creek Mining Company, Operating Properties Division, 1606 Hobart Building, San Francisco, Calif. He will continue his residence in San Francisco. He is succeeded by ALLAN JAMES whose headquarters will be in Salt Lake City.

The Alberta Society of Petroleum Geologists will be host to a Regional Meeting, the central theme of which, "Frontiers of Exploration in Canada," will emphasize oil and gas exploration. Technical Sessions will be on May 26 and May 27 and will explore the Geographical, Geological and Technological frontiers. Headquarters will be at the Banff Springs Hotel.

JOHN STAFFORD BROWN, Chief Geologist of the St. Joseph Lead Company, was awarded the Penrose Medal of the Society of Economic Geologists at the Annual Luncheon of the Society held in conjunction with its meeting with the A. I. M. E. in New York in February.

A. I. LEVORSEN, consulting geologist, Tulsa, Oklahoma, has been elected to honorary membership in the Society of Economic Paleontologists and Mineralogists.

BERNARD J. O'NEILL, JR. has joined the staff of Stanford Research Institute in Menlo Park, California, as a geologist, where he will be assigned to a study of the geology and hydrology of San Clemente Island.

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